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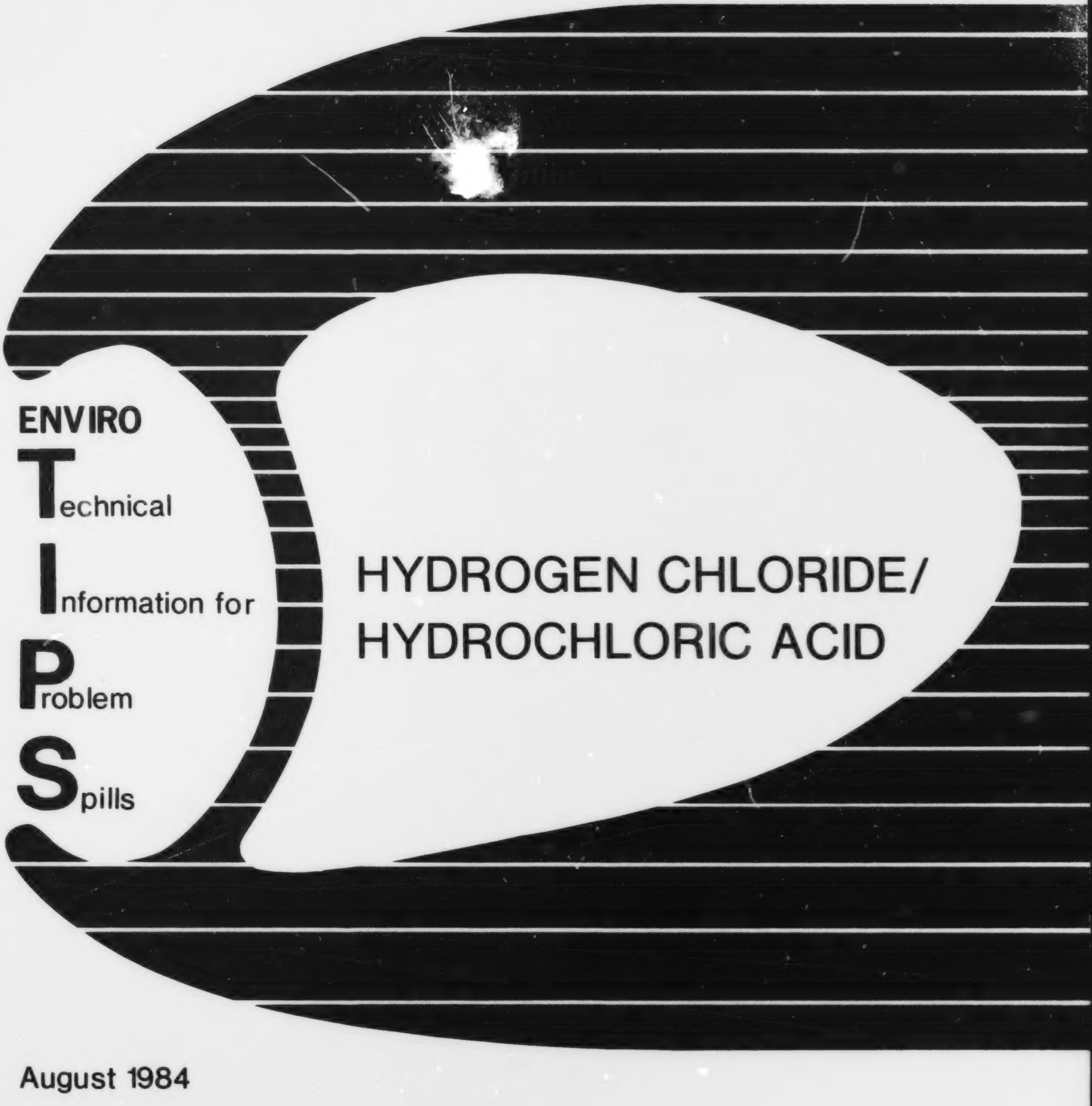

ENVIRO
Technical
Information for
Problem
Spills

HYDROGEN CHLORIDE/ HYDROCHLORIC ACID

August 1984

Canada

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

HYDROGEN CHLORIDE/HYDROCHLORIC ACID

TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations, and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

HYDROGEN CHLORIDE (HCl)/HYDROCHLORIC ACID (HCl aq.)

Colourless to pale yellow liquefied gas or liquid with a sharp irritating odour

SYNONYMS

Hydrochloric Acid (anhydrous), Muriatic Acid, Spirits of Salt, Chlorohydric Acid, Acide Hydrochlorique (Fr.)

IDENTIFICATION NUMBERS

UN No. 1050 (anhydrous), 2186 (refrigerated liquid acid); CAS No. 7647-01-0; OHM-TADS No. 7216748; STCC No. 4904270 (anhydrous), 4930228 (refrigerated liquid acid)

GRADES & PURITIES

Anhydrous:	99 percent
Acid:	18°Be - 27.9 percent 20°Be - 31.5 percent 22°Be - 35.2 percent

IMMEDIATE CONCERNS

Fire: When heated, toxic and corrosive hydrogen chloride gas is released from the acid and liquefied anhydrous product

Human Health: Moderately toxic by all routes. Highly corrosive to living tissues

Environment: Harmful to aquatic life, in some species at concentrations as low as 3.6 mg/L. The lower survivability limit for most fish is pH 5

PHYSICAL PROPERTY DATA

	Anhydrous	Hydrochloric Acid		
		18°Be	20°Be	22°Be
Shipping State:	liquid (liquefied compressed gas)	liquid	liquid	liquid
State: (@15°C, 1 atm):	gas	liquid	liquid	liquid
Boiling Point:	-85.05°C	form common boiling mixture of 20.22 percent at 108.6°C		
Melting Point:	-114.22°C	-62°C	-42°C	-35°C
Flammability:	not combustible	not combustible		
Vapour Pressure:	4330 kPa (21.1°C)	1.87 kPa	3.2 kPa	13.3 kPa (20°C)
Specific Gravity of Liquid (water =1):	1.05 (-155°C)	1.15	1.16	1.18 (20°C)
Solubility (in water):	50.6 g/100 mL @ 20°C	completely miscible		

	Anhydrous	Hydrochloric Acid		
		18°Be	20°Be	22°Be
Behaviour (in water):	boils, sinks and mixes, with evolution of heat	sinks and mixes, with evolution of heat		
Behaviour (in air):	vaporizes rapidly			
Odour Threshold Range:	0.13 to 10 ppm			
Odour Threshold:	1 to 5 ppm			

ENVIRONMENTAL CONCERNS

Harmful to aquatic life in low concentrations. All life forms are threatened by hydrogen chloride toxicity, due primarily to its acidity. There is no potential for bioaccumulation or food chain contamination

HUMAN HEALTH

TLV®: 5 ppm (7 mg/m^3)
IDLH: 100 ppm (anhydrous)

Exposure Effects

Inhalation: Inhalation of vapour and aerosol produces severe irritation of the upper respiratory tract, coughing, burning of throat, and choking. Extreme exposures can result in respiratory problems and death

Contact: Severe irritation and burning of eyes and lids. Visual impairment may result. Contact to skin may cause serious burns

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE". Notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and inhalation of vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible. Cool fire-exposed containers with water spray. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Remove material with pumps or vacuum equipment. Absorb small amounts of spill with sawdust, sand or synthetic sorbents, shovel into containers with covers. Neutralize contaminated soil with lime (calcium hydroxide)

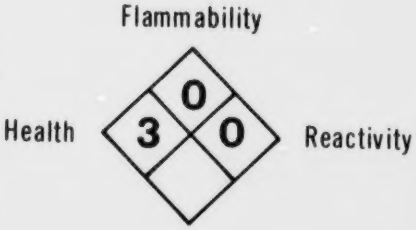
Water: Contain discharge by damming or water diversion. Neutralize with lime. Dredge or vacuum pump to remove contaminated bottom sediments

Air: Use water spray or fog to knock down and disperse vapours. Control runoff for later treatment and/or disposal

NAS HAZARD RATING

Category	Rating	
	Anhydrous	Acid
Fire	0	0
Health		
Vapour Irritant	4	3
Liquid or Solid Irritant	3	3
Poison	3	2
Water Pollution		
Human Toxicity	2	2
Aquatic Toxicity	2	2
Aesthetic Effect	2	2
Reactivity		
Other Chemicals	4	3
Water	2	0
Self-reaction	0	0

NFPA
HAZARD
CLASSIFICATION
Hydrochloric Acid



2 PHYSICAL AND CHEMICAL DATA

	Hydrogen Chloride	Hydrochloric Acid		
		18°Be	20°Be	22°Be
Physical State Properties				
Appearance	Colourless gas, which fumes in moist air (HCG 1981)	White to yellow clear liquid (Dow MSDS 1978, 1979a, b, 1980) (Colour is due to impurities (Fe, Cl_2, organics)) (Merck 1983)		
Usual shipping state(s)	Liquid, liquefied compressed gas (HCG 1981)	Liquid (MCA 1970)		
Physical state at 15°C, 1 atm	Gas	Liquid		
Melting point	-114.22°C (Kirk-Othmer 1980)			
Freezing point		approx. -62°C (est. from Linke 1958)	-42°C	-35°C
Boiling point	-85.05°C (Kirk-Othmer 1980)	Commercial solutions of HCl approach a constant boiling mixture containing 20.22 percent HCl and boils at 108.584°C (Sp. Gr. = 1.0959 (25°C) (Kirk-Othmer 1980)		
Vapour pressure	4330 kPa (21.1°C) (Matheson 1980)	1.87 kPa (20°C) (PPG 1979)	3.2 kPa (20°C)	13.3 kPa (20°C)
Decomposition temperature	1782°C (HCG 1981) Percent dissociation at various temperatures is as follows: 4.5 x 10-7 @ 25°C 0.342 @ 800°C 2.74 @ 1573°C 5.55 @ 2000°C 8.73 @ 2500°C 14.7 @ 3727°C (PPG 1979)			
Densities				
Specific gravity (20°/20°C)	1.267 (25°C) (air = 1) (Matheson 1980)	1.1417 (20°C) (water = 1) (Kirk-Othmer 1980)	1.1600	1.1789
		1.1391 g/mL (20°C) (CRC 1980)	1.1594 g/mL	1.1752 g/mL

	Hydrogen Chloride	Hydrochloric Acid		
		18°Be	20°Be	22°Be
Density				
	Gas: 1.6391 kg/m^3 (0°C) (Raznjevic 1976) 1.500 kg/m^3 (25°C) (Matheson 1980)			
	Liquid: 1.045 g/mL (-155°C) (Kirk-Othmer 1980) 1.480 g/cm^3 (-174.5°C) (cubic form)			
	Solid: 1.507 g/cm^3 (-192.2°C) (rhombic form) (Kirk-Othmer 1980)			
Fire Properties				
Flammability	Not combustible (NFPA 1978)	Not combustible (Du Pont MSDS 1979)		
Dissociation energy	431.62 kJ (25°C) (Kirk-Othmer 1980)			
Dissociation products	Hydrogen and chlorine			
Behaviour in a fire	At temperatures above 600°C, reacts significantly with metals and dissociates significantly. The resulting hydrogen is flammable and explosive (Kirk-Othmer 1980)	Liberates hydrogen on contact with metals which may result in a fire or explosion when ignited (MCA 1970)		
Other Properties				
Molecular weight of pure substance	36.46 (CRC 1980)		-	
Constituent components of typical commercial grade	Technical: 99 percent HCl minimum (Dow MSDS 1980) Electronic: 99.99 percent HCl minimum (Linde 1981)	27.92 percent HCl (Kirk-Othmer 1980)	31.45 percent HCl	35.21 percent HCl
Refractive index	Liquid: 1.254 (10°C) Gas: 1.0004456 (0°C)	1.3976 (20°C) (CRC 1980)	1.4066	1.4140
Viscosity (mPa•s)	Liquid: 0.405 (-15.5°C) (Kirk-Othmer 1980) Gas: 0.0131 (0°C) (Kirk-Othmer 1980); 0.0148 (25°C) (Matheson 1980); 0.0253 (25°C) (Kirk-Othmer 1980)	1.62 (CRC 1980)	1.80	2.0

	Hydrogen Chloride	Hydrochloric Acid		
		18°Be	20°Be	22°Be
Hygroscopicity	Very hygroscopic (MCA 1970)	Hygroscopic (MCA 1970)		
Latent heat of fusion	54.646 kJ/kg (-114.22°C) (Kirk-Othmer 1980)			
Latent heat of sublimation	527.2 J/g (20°C) (Perry 1973)			
Latent heat of vaporization	442.73 kJ/kg (-85.05°C)			
Heat of formation	-92.31 kJ/mole (25°C) (JANAF 1971)			
Ionization potential	Gas: 12.74 eV (Rosenstock 1977)	In water: 20.51 J (0.2 eV) (Kirk-Othmer 1980)		
Heat of solution	-74.8 kJ/mole (25°C) (CRC 1980)			
Heat capacity				
constant pressure (C_p)	Gas: 0.7998 kJ/(kg·C) (0°C); 0.8380 kJ/kg (700°C) (Kirk-Othmer 1980)			
constant volume (C_v)	Liquid: 1.656 kJ/(kg·°C) (-110°C); 0.58 kJ/(kg·°C) (HCG 1981)			
C_p/C_v (γ)	1.404 (0°C) (Kirk-Othmer 1980)			
Critical pressure	8316 kPa (Kirk-Othmer 1980)			
Critical temperature	51.54°C (Kirk-Othmer 1980)			
Triple point	-114.25°C (Kirk-Othmer 1980)			
Coefficient of thermal expansion x 10^{-3}/°C (20°C)	3.72 (Perry 1973) 3.77 (constant pressure, 0°C) (CRC 1957) 3.734 (constant volume, 0-100°C) (CRC 1957)	0.455 (33.2 percent solution, cubical) (Lange's Handbook 1979)		
Thermal conductivity	Liquid: 335 mW/(m·K) (-155°C) Gas: 13.4 mW/(m·K) (0°C)(Kirk-Othmer 1980)	9.8 mW/(m·K) (Lange's Handbook 1979)	4.4 mW/(m·K)	
Saturation concentration (calc.)	5840 g/m^3 (-51°C) (CRC 1980)			

	Hydrogen Chloride	Hydrochloric Acid		
		18°Be	20°Be	22°Be
Diffusivity	3.10×10^{-5} cm^2/s (in water 25°C, 0.1 M) (Perry 1973) 3.436×10^{-5} cm^2/s (in water, 25°C, 1 M) (CRC 1982)			
pH of aqueous solution		1.1(0.1 N solution, 25°C) 0.1 (1 N solution, 25°C) (CRC 1982)		
Eutectic compositions	24.8 percent aqueous solution (f.p.-86°C) (Lange's Handbook 1979)			
Dipole moment	3.74 C·m (Kirk-Othmer 1980)			
Surface tension	23 mN/m (-155°C) (Kirk-Othmer 1980) 24.718 mN/m (-92.9°C) (Matheson 1980) 71.75 mN/m (16.97 percent solution) 70.55 mN/m (23.74 percent solution) 65.75 mN/m (35.29 percent solution) (CRC 1982)			
Dielectric constant	Liquid: 14.2 (-114.22°C) Gas: 1.0046 (25°C) (Kirk-Othmer 1980)			
Electrical conductivity	1.7×10^{-7} ohm^{-1} m^{-1} (-114.22°C) 3.5×10^{-7} ohm^{-1} m^{-1} (-87.6°C)			
Solubility				
In water	82.3 g/100 mL (0°C) (CRC 1980) 50.6 g/100 mL (20°C) (Dow MSDS 1980) 67.3 g/100 mL (30°C) (CRC 1980) 63.3 g/100 mL (40°C) (CRC 1980) 59.6 g/100 mL (50°C) (CRC 1980) 56.1 g/100 mL (60°C) (CRC 1980)			
In other common materials	soluble in ethanol, diethyl ether and benzene (CRC 1980)			

Substance	Solubility (g/100 g)	Temperature
n-Hexane	0.71	-
n-Hexadecane	0.33	27°C
	0.22	102°C
Benzene	0.2	20°C
	0.125	40°C
Toluene	0.213	20°C
Methanol	109.2	0°C
	87.7	20°C
	68.8	40°C

Substance	Solubility (g/100 g)	Temperature
Ethanol	83.8	0°C
	75.6	10°C
	68.1	20°C
	61.0	30°C
Diisosopropyl Ether	34.9	10°C
Dibutyl Ether	25.0	10°C
Dioxane	43.3	10°C
Tetrahydrofuran	58.4	10°C
Chloroform	0.85	15°C
	0.69	25°C
Carbontetrachloride	0.60	20°C
	0.39	50°C

(Ullmann 1975)

Vapour Weight to Volume Conversion Factor

1 ppm = 1.487 mg/m^3
(20°C) (Verschueren 1977)

General Comments Concerning the Properties of Anhydrous Hydrogen Chloride and Hydrochloric Acid

Anhydrous hydrogen chloride is a colourless gas that can be condensed to a colourless liquid and frozen to a white crystalline solid. The gas is sometimes described as strong-smelling and pungent. It fumes in air. Gaseous hydrogen chloride is thermally stable, as shown in the following table for dissociation to the elements:

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

Temperature (K)	Percent Dissociation (calculated values)
298	4.5×10^{-7}
473	4.5×10^{-4}
673	1.5×10^{-2}
873	0.10
1073	0.342
1273	0.73
2273	5.55
4000	14.7

The dissociation of the gas into its elements is important in selecting materials of construction because the free chlorine formed is the corrosive agent. Under normal conditions, the anhydrous gas can be transmitted in mild steel piping over moderate distances with no difficulty. At temperatures much above 600°C (873 K), reactions with metals become important. It is assumed these reactions are the result of free chlorine formed by dissociation or by oxidation of HCl by contaminating air

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$$

The corrosion rate of mild steel by anhydrous hydrogen chloride at 300°C is reported as 0.25 cm/yr; no ignition has been observed at 760°C. Water vapour does not affect the corrosion rate of metals as long as no adsorbed moisture film can form. Generally, a temperature of 130°C or above at atmospheric pressure can be used for all mixtures of hydrogen chloride gas and water vapour. The reaction of the anhydrous gas with metals, although thermodynamically predicted for most metals but practically very slow, is depicted by the equation

$$M + nHCl \rightarrow MCl_n + n/2H_2$$

It has been reported to react with powdered silicon at 250°C to give trichlorosilane ($HSiCl_3$) and silicon tetrachloride ($SiCl_4$), and with the vapours of sodium and of potassium.

Liquid hydrogen chloride exists in a very narrow temperature range (29°C @ 101 kPa) and is thought to exhibit only limited hydrogen bonding.

$$3HCl \rightleftarrows H_2Cl^+ + HCl_2^-$$

Self-ionization occurs only to a very small extent. There have been no salts isolated of the former species, but some of the latter are known, e.g. $3CsX{\cdot}H_3O^+{\cdot}HCl_2^-$.

Its dielectric constant changes with temperature and is low in comparison with that of other solvents with a similar good ionizing power. Many organic compounds form conducting solutions in liquid hydrogen chloride. Because of the narrow temperature range of its liquid phase and the low temperatures required for liquifaction, however, studies in solutions of this material have been severely limited.

Solid hydrogen chloride consists of zigzag chains of hydrogen-bonded molecular crystals. Proton nuclear magnetic resonance studies at low temperatures have also shown the existence of a dimer, $(HCl)_2$. Three crystalline solid forms exist, two cubic and one rhombic, with densities of 1.469 (-166.15°C) and 1.48 g/cm^3 (-174.79°C) for the former two and 1.507 g/cm^3 (-192.15°C) for the latter. The latter form is ferroelectric (a crystalline material that over certain limited temperature ranges has a natural or inherent deformation (polarization) of the electrical fields or electrons associated with the atoms and groups in the crystal lattice. This results in the development of positive and negative poles, and a consequent direction of polarization which can be reversed when the crystal is exposed to an external electric field).

The vapour pressures of solid and liquid hydrogen chloride are expressed by the equation

$$\mathrm{Log}_{10}P(\mathrm{kPa}) = -k/T^n + 6.628$$

where k and n are equal to 1966.3 and 1.1600, respectively, for the solid and 945.7 and 1.0160, respectively, for the liquid. The specific heat for the gas is expressed by the equation

$$Cp = a + bT + cT^2 \text{ (in joules)}$$

where the values for a, b, and c are 28.1663, 1.8096×10^{-3} and 15.4692×10^{-7}, respectively.

Hydrogen chloride is extremely soluble in water. Its solutions deviate from both Raoult's and Henry's laws, the latter at all measured concentrations. The former law states that the vapour pressure of a substance, in equilibrium with a solution containing the substance, is equal to the product of the mole fraction of the substance in the solution, and the vapour pressure of the pure substance at the temperature of the solution (the law is not applicable to most solutions, although some conform closely). The latter law states that when a liquid and a gas remain in contact, the weight of the gas that dissolves in a given quantity of liquid is proportional to the pressure of the gas above the liquid. The solubilities at various temperatures and the vapour pressures and vapour compositions are shown elsewhere in this manual.

The gas and water form four hydrates. The monohydrate ($HCl{\bullet}H_2O$) melts at -15.35°C and is built of layers very similar to those in elementary arsenic, with the O and Cl atoms alternating. The units presumably are Cl^- and H_3O^+ ions. The dihydrate ($(H_2O)_2H^+Cl^-$, verified by X-ray analysis) is formed when a saturated solution is cooled at atmospheric pressure. It dissociates at -18.3°C in an open vessel and has a melting point of -17.7°C in a sealed tube. The trihydrate ($HCl{\bullet}3H_2O$) melts at -24.9°C; a very unstable hexahydrate ($HCl{\bullet}6H_2O$) melts at -70°C. Starting with pure water, addition of hydrogen chloride lowers the freezing point until a eutectic temperature of about -85°C is reached at 25 percent hydrogen chloride (a concentration that closely corresponds to the composition of the hexahydrate, 25.24 percent). Continued addition of the gas raises the freezing point first to that of the trihydrate and subsequently to that of the dihydrate and similarly to the monohydrate. Continued addition of HCl results in the separation of water and acid layers. This occurs at a temperature of -15.35°C and at a concentration of 66.8 percent. No stable homogenous solutions occur between 66.8 percent and

100 percent (pure HCl). In addition to forming hydrates, constant boiling mixtures are formed. At atmospheric pressure, the mixture boils at 108.584°C; its density at 25°C is 1.0959; the weight percent of hydrogen chloride is 20.222 (mole ratio $H_2O/HCl = 7.99$).

The gas is essentially completely ionized in aqueous solutions of all but the highest concentrations

1) $HCl(g) \rightleftarrows H^+(aq.) + Cl^-(aq.)$ $\Delta H° = -2110.9$ kJ/kg (infinite dilution, 25°C, 101.3 kPa)
2) $HCl(aq.) \rightleftarrows H^+(aq.) + Cl^-(aq.)$ $\Delta H° = -1616.5$ kJ/kg (infinite dilution, 25°C, 101.3 kPa)

The viscosity of hydrochloric acid solutions increases slightly with increasing concentration. It is related to the molar concentration, c, by the following equation:

$$(\eta - \eta_o)\ \eta_o = 0.0030 + 0.0620C^{0.5} + 0.0008c$$

where η_o is the viscosity of water at 25°C (0.8904 mPa•s). The surface tension of dilute hydrochloric acid solutions, only slightly less than that of water at 25°C (71.97 mN/m), declines slowly as the concentration is raised. The dielectric constant decreases slightly from that of water at 25°C (78.30) as the hydrogen chloride concentration increases until it reaches a minimum at 0.2 percent hydrogen chloride, at which point it rises slowly to a value somewhat above that of water as the concentration increases. The specific heat of aqueous hydrogen chloride decreases with decreasing temperature for a given percentage of hydrogen chloride and decreases with increasing percentage of hydrogen chloride for a given temperature. Equivalent conductivity of aqueous hydrogen chloride increases with temperature for a given concentration and decreases with increasing concentration for a given temperature.

Hydrogen chloride can react by either heterolytic or homolytic fission of the H-Cl bond; however, because the kinetic barrier to either type of fission is high for the anhydrous material, it is relatively inert. In the former type of fission reaction, the bond is broken unsymmetrically (electrons remain coupled); in the latter type, the bond is broken symmetrically (electron pairs are divided). Examples are H^+ and Cl^- for the former and H• and Cl• for the latter. Some typical reactions of the anhydrous material are briefly outlined below:

1. Reaction with Group V hydrides (NH_3, PH_3AsH_3) –

   $MH_3 + HCl \rightarrow MH_4^+ + Cl^-$

2. Reaction with nitrides, borides, silicides, germanides, carbides and sulphides – these reactions take place at a significant rate at temperatures of 650°C or above. The

products are the metal chlorides and the corresponding hydrides, e.g., NH_3, H_2S, etc.

3. Reaction with silicon, germanium and boron hydrides —

   $MH_4 + HCl \rightarrow MH_3Cl + H_2$

   $MH_3Cl + HCl \rightarrow MH_2Cl_2 + H_2$

   Complete substitution of chloride may be afforded, e.g., $SiCl_4$.

4. Reaction with metal oxides — the reaction with the transition metal oxides has been studied extensively; temperatures of 300°C or greater are required. Many other metal oxides also react in a similar manner. The products are the metal chlorides or oxychlorides, and water.
5. Reaction with metals was discussed earlier.
6. Reaction with oxidizing agents — the reaction with oxygen was discussed earlier in conjunction with the reaction with metals; however, other oxidizing agents also react with the material, e.g., MnO_2.
7. Reaction with other inorganic halogen compounds — addition compounds are formed with hydrogen bromide (HBr), iodide (HI) and cyanide (HCN) at low temperatures. These compounds are unstable at room temperature.
8. Reaction with oxyacids and their salts — reaction with sulphur trioxide gives liquid chlorosulphuric acid ($ClSO_3H$). Reaction with nitric acid liberates chlorine. Anhydrous sulphates of the heavy metals form addition compounds, generally with two moles of HCl, e.g., $CuSO_4 \cdot 2HCl$. The HCl is released at elevated temperatures.
9. Reaction with organic compounds — hydrogen chloride adds to carbon-carbon double and triple bonds in a variety of organic compounds. In addition, hydrogen chloride replaces aliphatic hydroxyl with chloride with the use of a liquid or solid catalyst:

   $$ROH + HCl \rightarrow RCl + H_2O$$

The reactions of hydrochloric acid are described below:

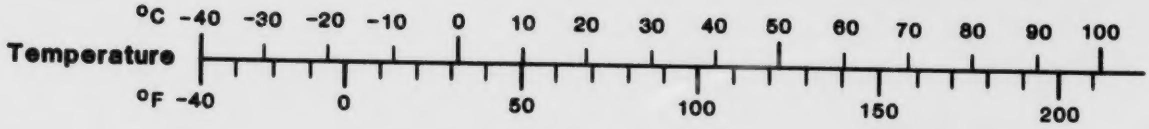
1. Reaction with metals — aqueous hydrochloric acid reacts with most metals and alloys

   $$M + nH_3O^+ \rightarrow M^{n+} + nH_2O + n/2H_2\uparrow$$

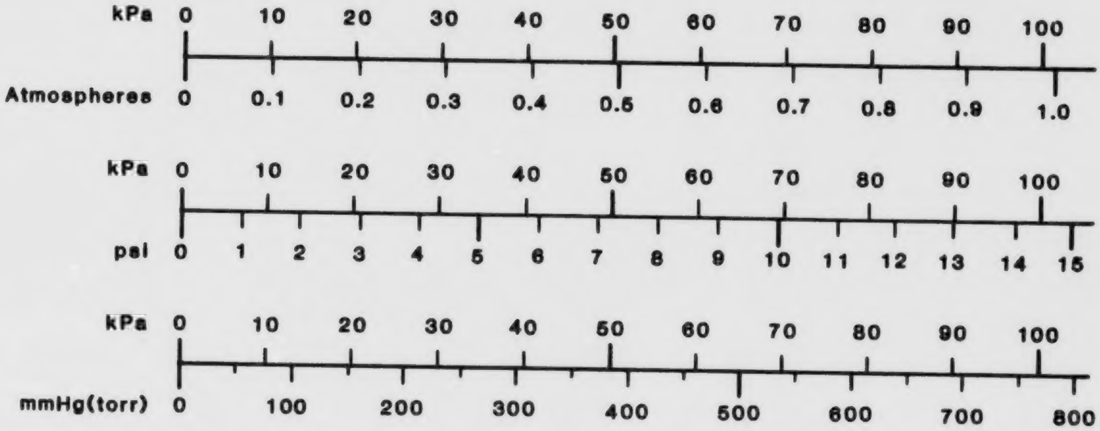
   The reaction rate depends on such variables as temperature and acid concentration, the presence of oxidizing, reducing, complexing or inhibiting agents, the presence of an oxide film, the prior history of the metal-treating process, the nature of the reacting species in alloys and composites, and the physical form of the metal.

2. Reaction with oxides and hydroxides — the reaction with aqueous solutions of alkali metal and alkaline earth hydroxides is a simple ionic salt-forming reaction. On the other hand, reactions with metal oxides and hydroxides of low solubility or insoluble in water are often complex, with rates depending on many factors similar to those noted for metals.
3. Reactions with oxidizing agents — aqueous hydrochloric acid can be oxidized to chlorine and water by various oxidizing agents such as hydrogen peroxide (H_2O_2), selenic acid (H_2SeO_4) and vanadium pentoxide (V_2O_5).

CONVERSION NOMOGRAMS


Temperature
°C -40 -30 -20 -10 0 10 20 30 40 50 60 70 80 90 100
°F -40 0 50 100 150 200

Pressure 1 kPa = 1,000 Pa


kPa 0 10 20 30 40 50 60 70 80 90 100
Atmospheres 0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
kPa 0 10 20 30 40 50 60 70 80 90 100
psi 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
kPa 0 10 20 30 40 50 60 70 80 90 100
mmHg(torr) 0 100 200 300 400 500 600 700 800

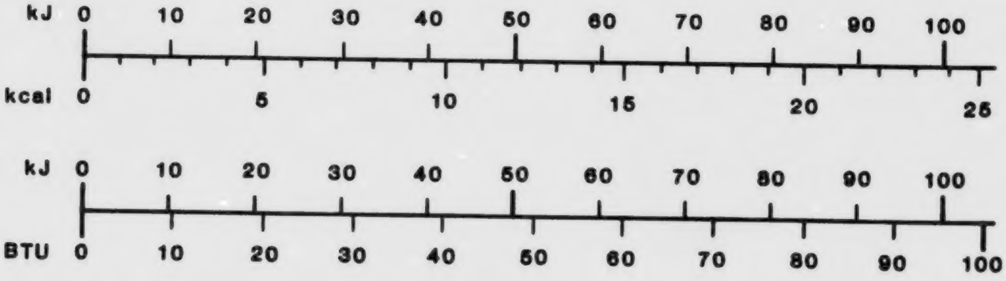
Viscosity

Dynamic 1 Pa·s = 1,000 centipoise (cP)

Kinematic 1 m²/s = 1,000,000 centistokes (cSt)

Concentration (in water)
1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1,000 J


kJ 0 10 20 30 40 50 60 70 80 90 100
kcal 0 5 10 15 20 25
kJ 0 10 20 30 40 50 60 70 80 90 100
BTU 0 10 20 30 40 50 60 70 80 90 100

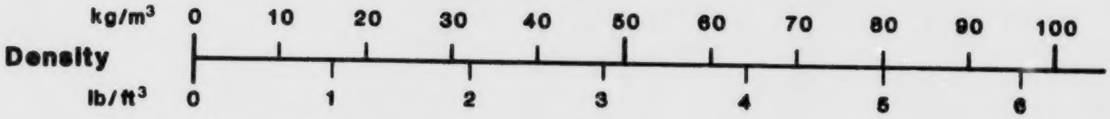

kg/m³ 0 10 20 30 40 50 60 70 80 90 100
Density
lb/ft³ 0 1 2 3 4 5 6

FIGURE 1

PHASE DIAGRAM OF THE $HCl \cdot H_2O$ SYSTEM

Reference: LINKE 1958; KIRK-OTHMER 1980; CRC 1980

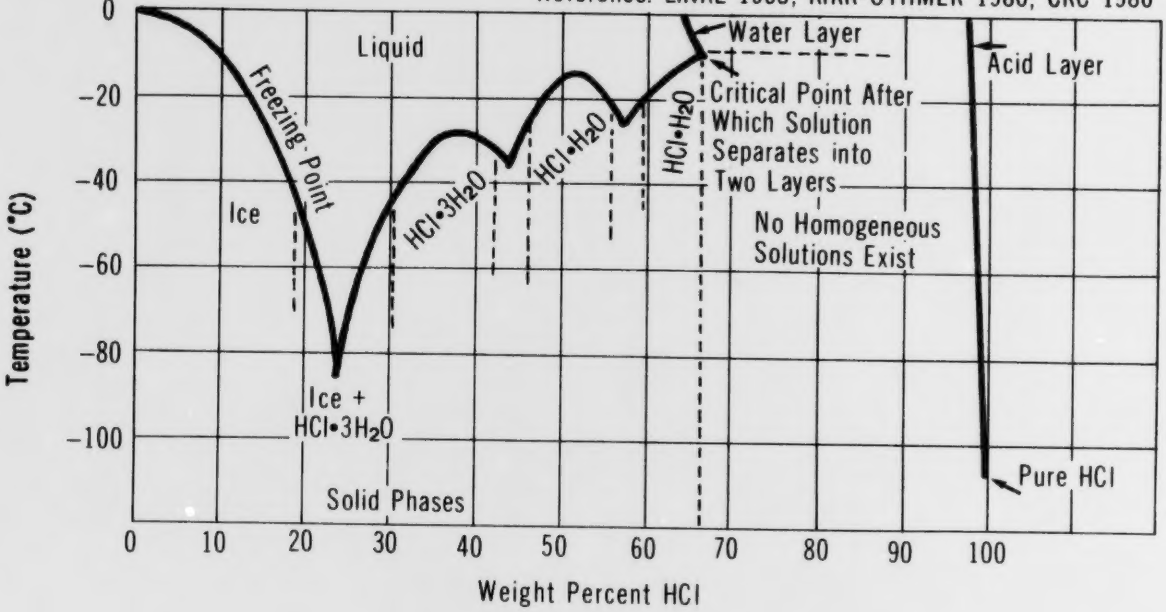


FIGURE 2

DENSITY OF SOLUTIONS

Reference: KIRK-OTHMER 1980

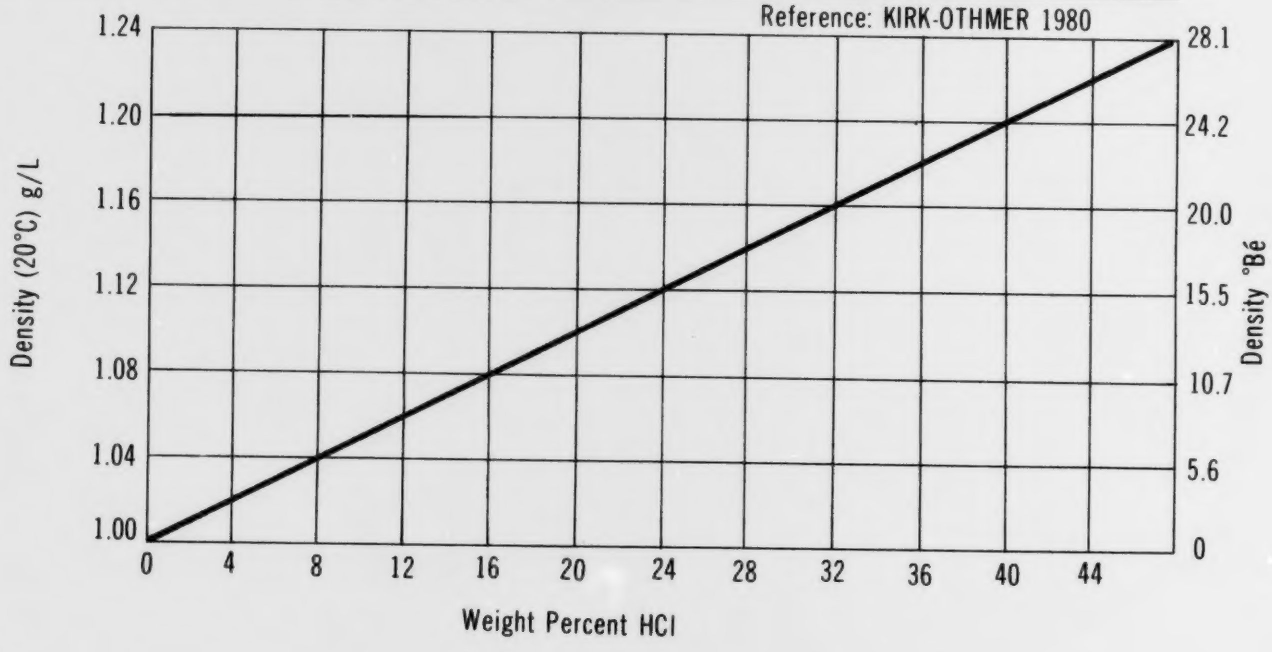


FIGURE 3

HYDROGEN CHLORIDE

VAPOUR PRESSURE VS TEMPERATURE

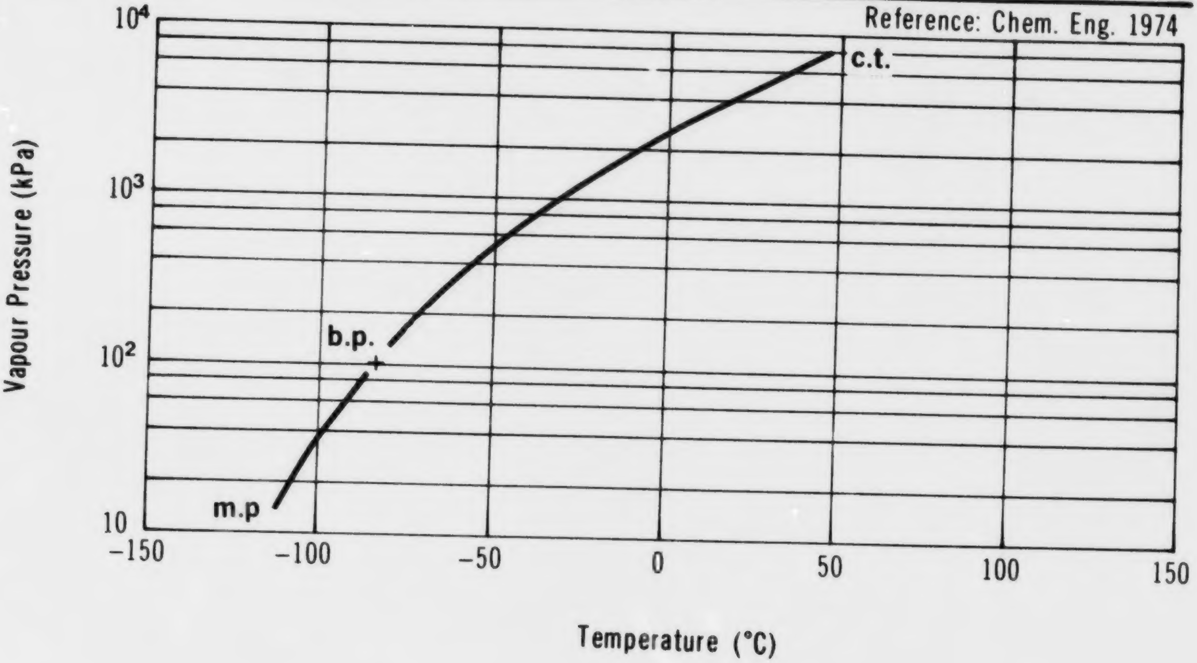


FIGURE 4

HYDROGEN CHLORIDE

LIQUID DENSITY vs TEMPERATURE

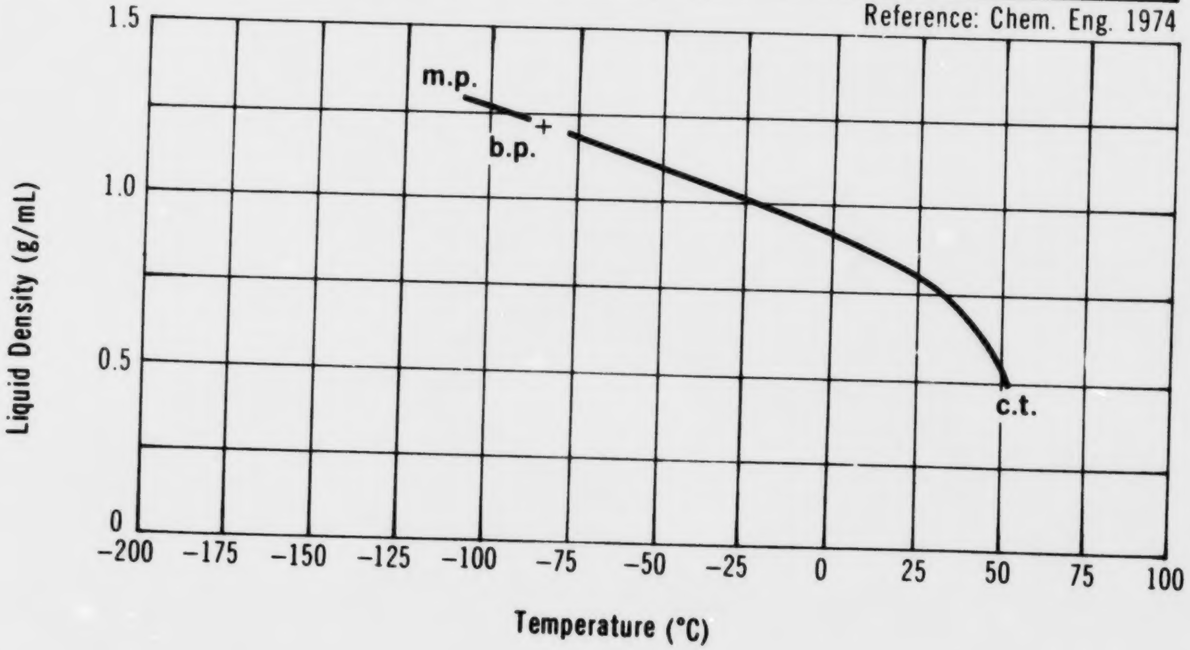


FIGURE 5

HYDROCHLORIC ACID

PERCENTAGE HCl IN VAPOUR

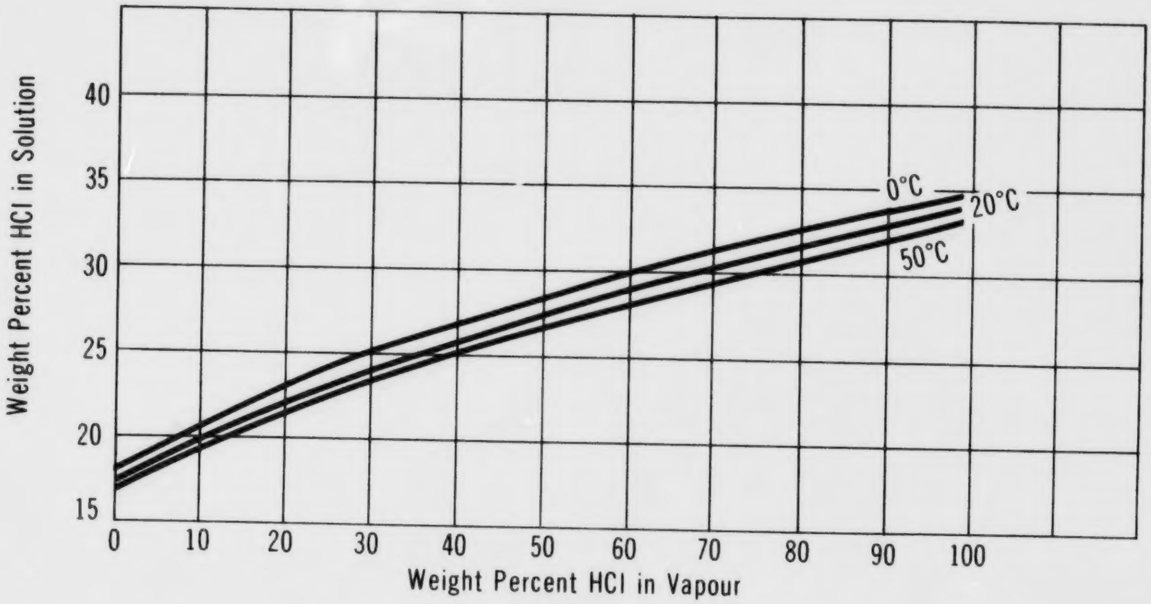


FIGURE 6

HYDROGEN CHLORIDE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

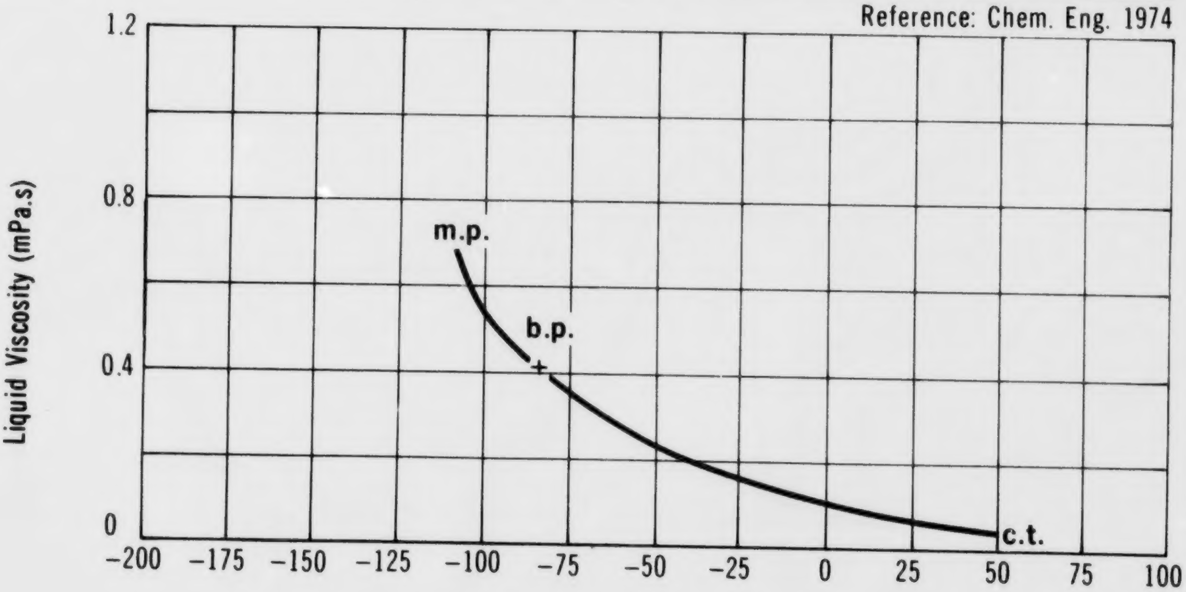


FIGURE 7

HYDROGEN CHLORIDE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

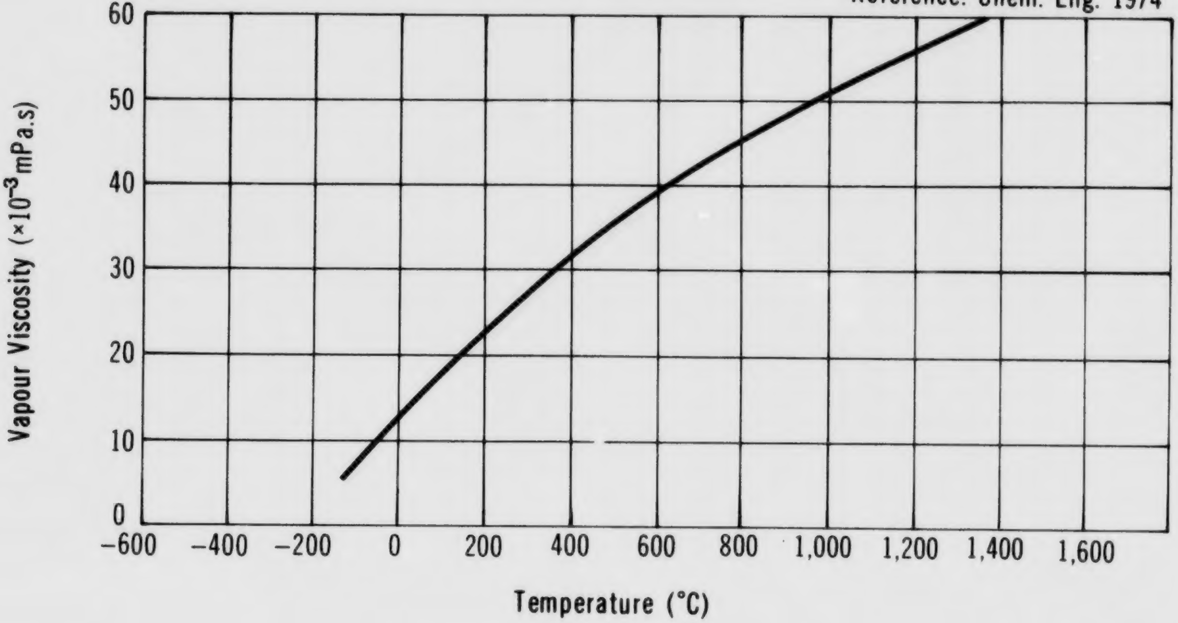
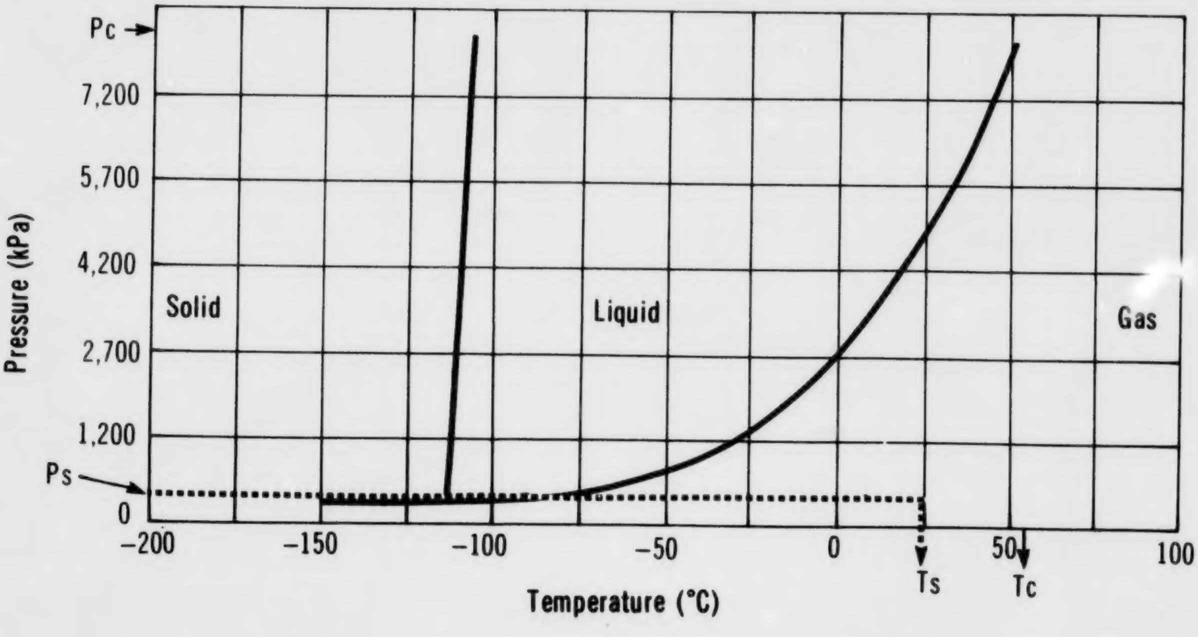


FIGURE 8

HYDROGEN CHLORIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

3.1.1 Anhydrous. Hydrogen chloride, anhydrous, is sold in a technical grade with a purity of greater than 99 percent, and in an electronic grade with a minimum purity of 99.99 percent (Air Products SGDS 1980; PC 1981).

3.1.2 Aqueous. Hydrochloric acid is sold as a liquid in the following strengths (Corpus 1983; PC 1981; Dow MSDS 1979a,b; PPG 1979; MCA 1970).

Grades	Strengths	Concentration
Commercial	18°Be	27.9 percent
Technical or Commercial	20°Be*	31.5 percent
Commercial	22°Be	35.2 percent
Food	20/22°Be	31.5/35.2 percent

* Most common grade sold.

3.2 Domestic Manufacturers (Corpus 1983; CCPA 1981; Scott 1979; CBG 1980)

These are corporate headquarters addresses and are not intended as spill response contacts.

Allied Chemical Canada Ltd.
201 City Centre Drive
Mississauga, Ontario
L5B 2T9
(416) 276-9211

Canadian Occidental Petroleum Ltd.
Hooker Chemical Division
700-4th Avenue S.W.
Calgary, Alberta
T2P 0K2
(403) 265-2390

Canso Chemicals Ltd.
P.O. Box 484
New Glasgow, Nova Scotia
B2H 5E5
(902) 755-1784

C-I-L Inc.
90 Sheppard Avenue East
Willowdale, Ontario
N2N 6H2
(416) 226-6110

Dow Chemical Canada Inc.
P.O. Box 1012
Modeland Road
Sarnia, Ontario
N7T 7K7
(519) 339-3131

Du Pont Canada Inc.
555 Dorchester Blvd. West
P.O. Box 6600
Montreal, Quebec
H3C 2V1
(514) 861-3861

FMC Canada Ltd.
570-885 Dunsmuir Street
Vancouver, British Columbia
V6C 1N5
(604) 685-6508

Great Lakes Forest Products
Duke Street
Dryden, Ontario
P8N 2Z9
(807) 223-2323

Prince Albert Pulp Company Ltd.
Saskatoon Chemicals Division
P.O. Box 1586
Saskatoon, Saskatchewan
S7K 3R3
(306) 652-9456

St. Anne Chemical Co.
8 Prince Arthur Avenue
Toronto, Ontario
M5R 1A9
(416) 968-2900

Uniroyal Ltd.
895 Don Mills Road
Don Mills, Ontario
M3C 1W3
(416) 446-5755

3.3 **Other Suppliers** (Corpus 1983)

Bartek Chemical Co. Ltd.
P.O. Box 609
Burlington, Ontario
L7R 3Y5
(416) 639-0807

Occidental Chemicals
(Shipped directly to customer from
Niagara Falls, New York)

Pennwalt of Canada Ltd.
700 Third Line
Oakville, Ontario
L6J 5A3
(416) 827-9841

Union Carbide Canada Ltd.
(for Hydrogen Chloride)
123 Eglinton Avenue East
Toronto, Ontario
M4P 1J3
(416) 487-1311

3.4 Major Transportation Routes

Current Canadian production of hydrogen chloride and hydrochloric acid is very widespread, occurring in seven provinces. The largest production facilities are located in Fort Saskatchewan, Alberta, in Sarnia, Ontario, and in Becancour, Quebec. Transportation of the products is very widespread.

3.5 **Production Levels** (Corpus 1983)

Company, Plant Location		Nameplate Capacity kilotonnes/yr (1982)
Allied Chemical Canada, Amherstburg, Ont.*		7
C-I-L, Becancour, Que.		35
C-I-L, Cornwall, Ont.*		8
Canadian Occidental Petroleum, N. Vancouver, B.C.*		8
Canso Chemicals, New Glasgow, N.S.*		1
Dow Chemical Canada, Ft. Saskatchewan, Alta.*		45
Dow Chemical Canada, Sarnia, Ont.		75
Du Pont Canada, Maitland, Ont.		8
FMC Chemicals, Squamish, B.C.*		12
Great Lakes Forest Products, Dryden, Ont.*		2
St. Anne Chemical, Nackawic, N.B.*		3
Saskatoon Chemical, Saskatoon, Sask.*		8
Uniroyal Chemical, Edmonton, Alta.		2
	TOTAL	214
Domestic Production (1982)		135.4
Imports (1982)		5.4
	TOTAL SUPPLY	140.8

* Primarily for captive use.

3.6 The Manufacture of Hydrochloric Acid

3.6.1 General. Hydrogen chloride can be prepared by a variety of methods. These include the pyrohydrolysis of such salts as calcium and magnesium chlorides, hydrolysis of metal chlorides such as titanium tetrachloride ($TiCl_4$) and by the thermal dissociation of various chloride hydrates made synthetically, such as aluminum trichloride hexahydrate ($AlCl_3 \cdot 6H_2O$). The commercially significant processes include the salt-sulphuric acid process, direct synthesis from hydrogen and chlorine, and as a by-product from the preparation of various organic compounds (Kirk-Othmer 1980).

3.6.2 Manufacturing Processes. In the salt-sulphuric acid process, the reaction takes place in two stages according to the equations

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$

Both reactions are endothermic, with the former taking place at about 150°C and the latter at about 550-600°C. Various types of furnaces, including cast iron retorts, the

Mannheim mechanical furnace (consisting of an enclosed stationary circular muffle with a concave bottom pan and a domed cover), and the Lawry furnace, are used for this process. The latter employs a horizontal two-chambered rotating cylinder for the reaction vessel. The most recent design is the Cannon fluid-bed reactor in which sulphuric acid vapours are injected with the combustion gases into a fluidized bed of salt. Potassium chloride has also been used as fuel in the Mannheim furnace.

In the Hargreaves Process, a variation of the Mannheim process, the reactants are salt, sulphur dioxide, air and water. The reaction is exothermic and self-sustaining once the reactants are preheated to the reaction temperature of 430-540°C. The basic reaction is

$$4NaCl + 2SO_2 + O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4HCl$$

The use of air, however, results in a product gas containing only 10-12 percent hydrogen chloride as compared to 30-60 percent in the off-gases from a Mannheim furnace process.

In the direct synthesis from hydrogen and chlorine, the reaction is highly exothermic. The equilibrium flame temperature for the adiabatic reaction of stoichiometric proportions of hydrogen and chlorine is 2490°C. The equilibrium mixture contains 4.2 percent free chlorine (as Cl_2) by volume at this temperature. As the gases are cooled, the free hydrogen and chlorine combine rapidly; at 200°C, the concentration of free chlorine is negligible. A burner gas containing over 99 percent hydrogen chloride can be obtained with proper control of the feed gases. A typical combustor installation contains a vertical water-cooled combustion chamber (usually fabricated from graphite) with the flame propagating from the bottom (older design) or with a downward-firing vessel (newer design). The gas is cooled in an external absorption train with upward-firing units; with downward firing units, the absorber is integral to the unit. The basic reaction in this process is

$$Cl_2 + H_2 \xrightarrow[>200°C]{} 2HCl$$

When prepared as a by-product from an organic synthesis reaction, the crude hydrogen chloride gas thus produced may be contaminated with unreacted chlorine and organics, chlorinated organics, impurities present in the various reactants, and entrained solids such as catalyst particles. Generally, hydrogen chloride prepared by this process is used captively. Many purification processes are available; the use of any specific one may depend on whether anhydrous hydrogen chloride or hydrochloric acid is the desired product.

Some of the purification processes are described very briefly in the following sections.

3.6.2.1 Removal of water. Small amounts of water can be removed from hydrogen chloride gas with sulphuric acid. Residual water content will be less than 0.02 percent. Larger amounts of water can be removed prior to treatment with sulphuric acid by cooling the gas mixture and thereby condensing out concentrated hydrochloric acid. Residual water can be lowered to less than 10 ppm by adding chlorosulphuric acid ($ClSO_3H$) to the sulphuric acid. The sulphuric acid mixture also removes unsaturated materials such as ethylene and vinyl chloride; sulphuric acid alone removes certain organic compounds such as monochloroacetic acid (ClH_2CCO_2H).

3.6.2.2 Removal of chlorine. Chlorine can be removed by adsorption on activated carbon or by reaction with an olefin such as ethylene over active carbon at a temperature of 30-200°C. Reaction of the contaminated gas with liquid high-boiling olefins can reduce the chlorine content to less than 0.01 percent.

3.6.2.3 Removal of organics. The use of selective solid adsorbents is effective. Aromatic compounds are effectively removed by polystyrene foam. Synthetic zeolites work well for toluene and chlorosilanes. Active carbon or charcoal are effective for chloroacetylenes; lower-boiling organic compounds can be removed by scrubbing with a high-boiling organic liquid.

Many other selective procedures for purifying hydrogen chloride are available. The reader is directed to Kirk-Othmer (1980) for a more complete listing.

3.7 Major Uses in Canada (Corpus 1983; Air Products SGDS 1980)

Hydrogen chloride (anhydrous) is used in the electronic, petroleum, steel mill pickling and other metal working industries.

Hydrochloric acid is used in the pulp and paper, brine purification, pharmaceutical, mining and metallurgical industries. It is also used in the chemical industry in the manufacture of ferric chloride, ethyl chloride and 1,1,1-trichloroethane. In 1982, 42 percent of domestic demand was used for brine purification, 12 percent for the manufacture of ethyl chloride, 9 percent for steel mill pickling and about 9 percent for the manufacture of ferric chloride.

3.8 Major Buyers in Canada

3.8.1 Hydrochloric Acid (Corpus 1983; CBG 1980).

A & B Chemical Products, Stouffville, Ont.
A & K Petro-Chem Industries, Weston, Ont.
Alcolac Ltd., Valleyfield, Que.
Algoma Steel, Sault Ste. Marie, Ont.
Anachemia, Montreal, Que.
Arliss Chemical, Montreal, Que.
Baldwin & Kroll, Edmonton, Alta.
Bartek Chemical, Burlington, Ont.
Bate Chemical, Toronto, Ont.
Benson Chemical, Freelton, Ont.
Beta Well Service, Edmonton, Alta.
Billiton Canada, St. George, N.B.
Borg-Warner, Calgary, Alta.
Canada Colours & Chemicals, Toronto, Ont.
Canadian Tungsten, Vancouver, B.C.
Capo Polishes, Burlington, Ont.
Diversey Environment, Mississauga, Ont.
Dofasco, Hamilton, Ont.
Dowell of Canada, Calgary, Alta.
Dustbane Enterprises, Ottawa, Ont.
Endako Mines, Endako, B.C.
Ethyl Canada, Sarnia, Ont.
Haliburton Services, Calgary, Alta.
Hanson Inc., Toronto, Ont.
Industrial Grain Products, Candiac, Que.
International Chemical, Brampton, Ont.
Kert Chemical, Toronto, Ont.
Nacan Products, Collingwood, Ont.
Nowsco Well Service, Calgary, Alta.
Pennwalt of Canada, Oakville, Ont.
Robinson & Webber, Winnipeg, Man.
St. Lawrence Starch, Mississauga, Ont.
Schlumberger of Canada, Calgary, Alta.
Shefford Chemicals, Granby, Que.
Stanchem, Montreal, Que.
Steel Co. of Canada, Hamilton, Ont.
Uba Chemical, Mississauga, Ont.
Winfield Chemical Ind., Woodstock, Ont.

3.8.2 Hydrogen Chloride, Anhydrous (CBG 1980).

Air Products, Brampton, Ont.
Canadian Liquid Air Co. Ltd., Toronto, Ont.
Matheson of Canada Ltd., Brampton, Ont.
Union Carbide Canada Ltd., Toronto, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Hydrochloric acid, aqueous, is shipped bulk in specially designed railway tank cars, tank motor vehicles and portable tanks.

Hydrogen chloride, anhydrous, is occasionally shipped under pressure as a liquid in railway tanks and highway tankers.

4.1.1.1 Railway tank cars. Railway tank cars used in the transportation of hydrochloric acid are described in Table 2 (RTDCR 1974).

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS FOR HYDROCHLORIC ACID

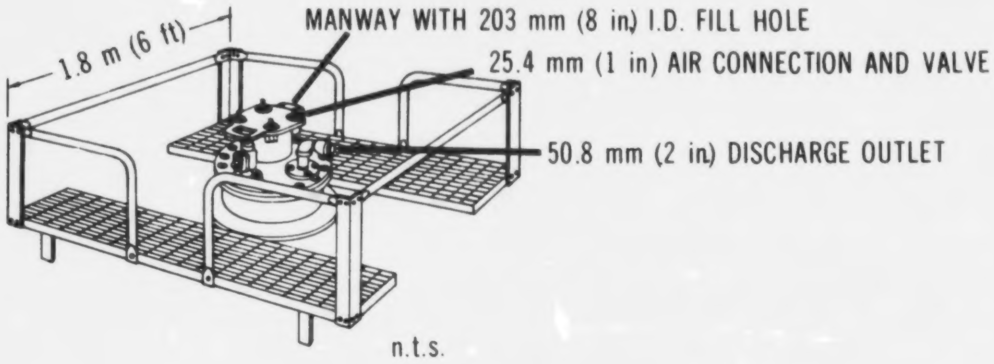
CTC/DOT* Specification Number	Description
103BW	Steel fusion-welded tank with dome. Uninsulated or insulated Rubber lined tank. 1% minimum outage. Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 414 kPa (60 psi). Safety vent at 414 kPa (60 psi) with frangible disc with 3 mm (1/8 in.) breather hole.
111A100W5	Steel fusion-welded tank without dome. Uninsulated or insulated. Rubber lined. 2% minimum outage. Gauging device. Top unloading arrangement required. Bottom outlet or washout prohibited. Test pressure 690 kPa (100 psi). Safety vent set at 690 kPa (100 psi) with frangible disc with 3 mm (1/8 in.) breather hole.

* Canadian Transport Commission and Department of Transportation (U.S.)

The acid is often shipped in CTC/DOT 111A100W5 railway tank cars as illustrated in Figure 9. Table 3 indicates railway tank car details associated with this drawing. Hydrochloric acid cars are never unloaded through bottom outlets; these are prohibited. The cars are unloaded from the top by pump or air padding (MCA 1970). The acid is withdrawn through an eduction pipe which extends from the bottom of the tank to

RAILWAY TANK CAR - CLASS 111A100W5

(Reference - CLC 1980, RTDCR 1974)


1.8 m (6 ft)
MANWAY WITH 203 mm (8 in) I.D. FILL HOLE
25.4 mm (1 in) AIR CONNECTION AND VALVE
50.8 mm (2 in) DISCHARGE OUTLET
n.t.s.

Detail of loading platform

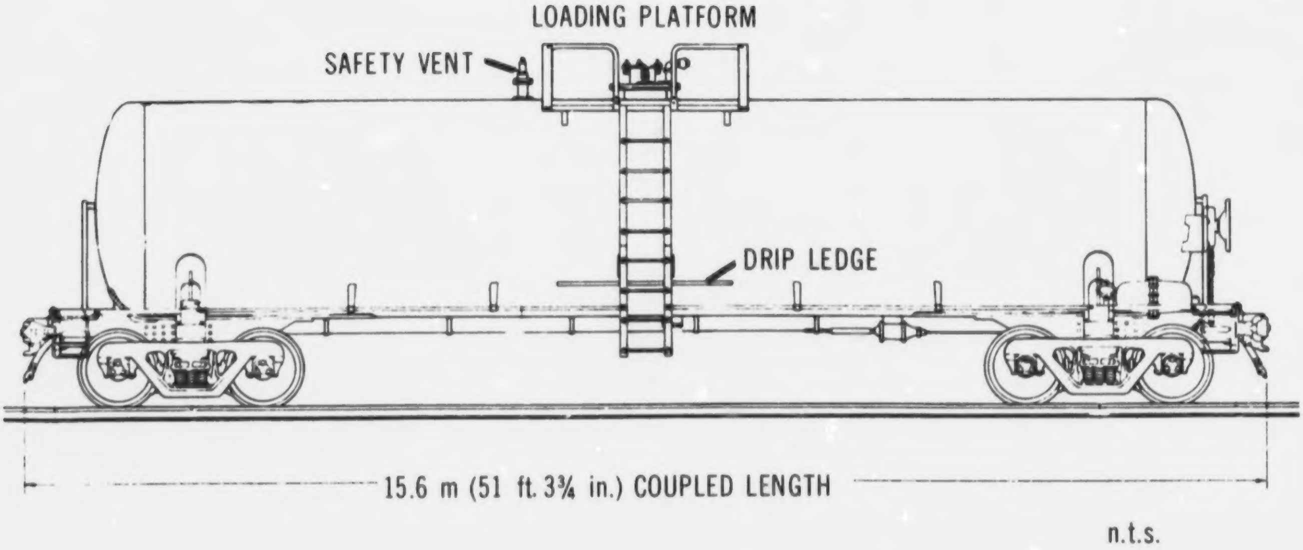

LOADING PLATFORM
SAFETY VENT
DRIP LEDGE
15.6 m (51 ft. 3¾ in.) COUPLED LENGTH
n.t.s.

Illustration of train car layout

TABLE 3 RAILWAY TANK CAR DETAILS - CLASS 111A100W5 (TCM 1979; RTDCR 1974)

	Description	Dimension	Notes
Overall	Nominal capacity	75 700 L (16 700 gal.)	
	Car weight-empty	25 200 kg (55 600 lb.)	
	Car weight-full	119 300 kg (263 000 lb.)	
Tank	Material	Steel	Rubber-lined 4.8 mm (3/16 in.)
	Thickness	11.1 mm (7/16 in.)	
	Inside diameter	2.74 m (108 in.)	
	Test pressure	690 kPa (100 psi)	
	Burst pressure	3450 kPa (500 psi)	
Typical Dimensions	Coupled length	15.6 m (51 ft. 3 3/4 in.)	
	Length over strikers	14.8 m (48 ft. 8 1/4 in.)	
	Length of truck centers	11.5 m (37 ft. 8 3/4 in.)	
	Height to top of grating	3.48 m (12 ft. 5 3/8 in.)	
	Overall height	4.56 m (14 ft. 11 3/8 in.)	
	Overall width (over grabs)	3.21 m (10 ft. 6 1/2 in.)	
	Coupler height over rail	0.88 m (2 ft. 10 1/2 in.)	
	Length of grating	2.44 m (8 ft. 1/8 in.)	
	Width of grating	1.83 m (6 ft.)	
Loading/ Unloading Fixtures	Unloading connection	51 mm (2 in.)	
	Fill hole	203 mm (8 in.)	
	Air connection	25 mm (1 in.)	
	Bottom outlet	Prohibited	
	Bottom washout	Prohibited	
Safety Devices	Safety vent		Required, must be equipped with frangible disc with 3 mm (1/8 in.) vent hole

the top operating platform where it terminates with a 51 mm (2 in.) unloading connection flange. Air pressure of 207 kPa (30 psi) is applied through the 25 mm (1 in.) air connection valve. A safety vent set at 690 kPa (100 psi) is required on top of the rail car. A gauging device, either the rod type or the tape type, is optional.

Hydrochloric acid is never transported under pressure. Railway tankers should be rubber-lined or lined with equally acid-resistant material. Safety valves of approved design must be used complete with frangible disc.

Railway tank cars transporting hydrogen chloride, anhydrous, are not covered in CTC/DOT regulations but shipments can be made in selected tank cars for this service (MCA 1970). Hydrogen chloride is shipped as a liquefied gas in insulated cars, usually under the CTC/DOT 105A600W specification. This type of car has a steel fusion-welded tank with a top loading arrangement. A bottom outlet or washout is prohibited. A safety valve set at 3100 kPa (450 psi) must also be employed (TCM 1979). Carbon or stainless steel can be used for the tanker provided that the type selected has good low temperature qualities. The top unloading arrangement on hydrogen chloride tank cars is very similar to that used on chlorine railway tankers.

4.1.1.2 **Tank motor vehicles.** Hydrochloric acid is shipped by tank motor vehicles of various capacities (MCA 1970).

Similar to railway tank cars, these highway tankers are unloaded from the top, usually with the standpipe being extended down over the back of the tank. Compressed air is used for unloading. The air inlet is usually a 25 mm (1 in.) diameter male threaded connection located at the top of the trailer through which air pressure not exceeding 207 kPa (30 psi) may be applied.

Tank motor vehicles must conform to Transport Canada Specification TC312, as outlined in Table 4. Hydrochloric acid solutions are not transported under pressure. Highway tankers must be pressure tested at 311 kPa (45 psi) minimum to allow for the compressed air pressure of 207 kPa (30 psi) used during top unloading. The maximum working pressure of the tanker is in effect 207 kPa (30 psi).

Hydrogen chloride, anhydrous, is transported in highway tankers similar to the railway tankers used for similar service. Under exemption of the DOT, hydrogen chloride is authorized for shipment in tank motor vehicles conforming to Transport Canada Specification TC331; that is, a seamless or welded steel tank, insulated, maximum design pressure of 3450 kPa (500 psi), and designed and constructed in accordance with the ASME Code (HCG 1981). Tanks are loaded with liquid hydrogen chloride at -56.6°C and 345 kPa (50 psi). Unloading must be started within 3 days unless special methods are used to keep truck pressure between 345 and 552 kPa (50 to 80 psi) (HCG 1981).

4.1.1.3 **Portable tanks.** Portable tanks have been used to transport small volumes of hydrochloric acid solutions. The capacities and weights of tanks vary depending on requirements of the user.

TABLE 4 TANK MOTOR VEHICLE SPECIFICATIONS FOR HYDROCHLORIC ACID

TC* Specification Number	Description
TC312 (MC312)	Steel butt-welded tank. Design and construct in accordance with ASME Code when unloading by pressure in excess of 103 kPa (15 psi). Gauging device not required. Top and/or bottom discharge outlet. Minimum one pressure relief device per compartment as required by ASME Code. One minimum 380 mm (15 in.) diameter manhole per compartment. Bottom washout optional.

* Transport Canada

Unloading fittings and methods are similar to those discussed for railway tank cars and highway tankers.

Portable tanks must conform to Transport Canada Specification TC60 described in Table 5 (TDGC 1980). Hydrogen chloride, anhydrous, is not shipped in portable tanks.

TABLE 5 PORTABLE TANK SPECIFICATIONS FOR HYDROCHLORIC ACID

TC* Specification Number	Description
TC60	Steel, fusion-welded or seamless. Design and construct in accordance with ASME Code. Tank and permanent attachments to be post-weld heat treated as a unit. 1% dome. Bottom discharge outlets prohibited except for acid and corrosive liquids. Bottom washout optional. Minimum one pressure relief device. Test pressure 414 kPa (60 psi).

* Transport Canada

4.1.2 **Packaging.** In addition to bulk shipments, hydrochloric acid is also transported in drums as listed in Table 6 (TDGC 1980). Steel drums may be lined with plastic or

TABLE 6 DRUMS FOR HYDROCHLORIC ACID

Type of Drum	Designation	Description	Figure No. (If Any)
Steel with rubber lining	1A1	Nonremovable head, reusable	10
	1A1A	1A1 with reinforced chime	10
	1A1B	1A1 with welded closure flange	10
	1A1C	1A1 with lead coating	10
	1A1D	1A1 with coating (other than lead)	10
	1A3	Nonremovable head Single use only	10
Plastic	1H1	Nonremovable head Maximum capacity 250 L (55 gal.) Maximum net mass 400 kg (880 lb.)	
Steel with inner plastic receptacle	6HA1	Outer steel sheet drum Inner plastic receptacle Maximum capacity 225 L (55 gal.)	

rubber to reduce corrosion. Glass carboys, boxed or in expanded polyethylene containers, are also used.

Hydrogen chloride, anhydrous, can be shipped in cylinders equipped with suitable safety devices and tested as per CTC/DOT regulations (MCA 1970). CTC specifications are listed in Table 7.

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Hydrochloric Acid Railway Tank Cars. Prior to off-loading, certain precautions must be taken:

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.
- The air padding system must be equipped with a pressure regulator to control the maximum air pressure applied to the car (CCPA 1982).
- A water-scrubber system should be provided to remove acid from the air, permitting depressurization of the car prior to closure (CCPA 1982).

FIGURE 10

TYPICAL DRUM CONTAINER

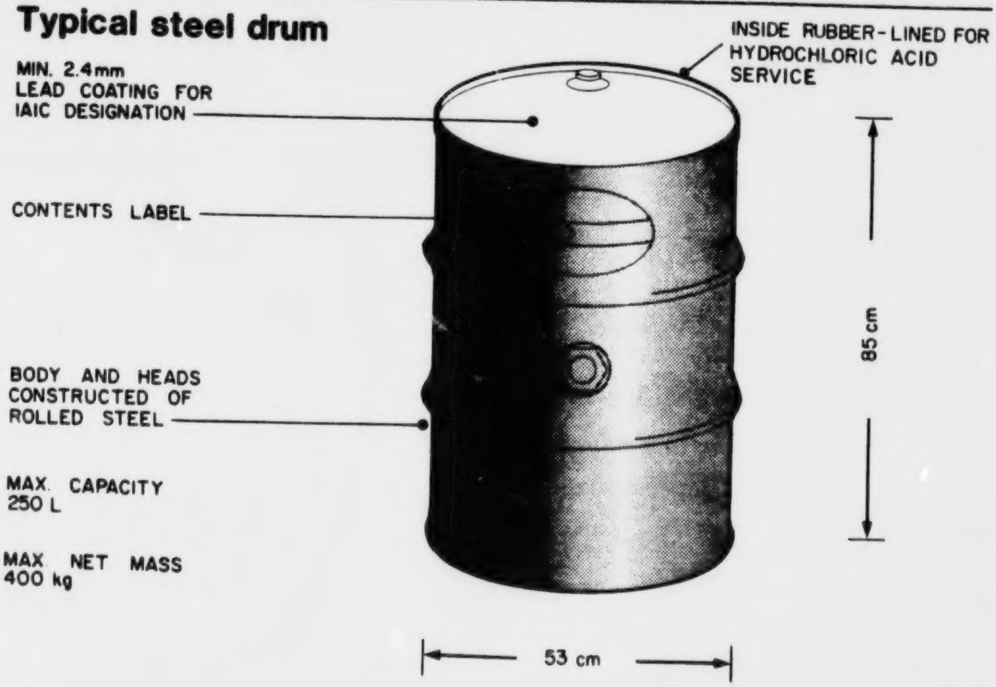

Typical steel drum
MIN. 2.4mm LEAD COATING FOR IAIC DESIGNATION
INSIDE RUBBER-LINED FOR HYDROCHLORIC ACID SERVICE
CONTENTS LABEL
BODY AND HEADS CONSTRUCTED OF ROLLED STEEL
MAX. CAPACITY 250 L
MAX NET MASS 400 kg
85 cm
53 cm

TABLE 7 CYLINDER SPECIFICATIONS FOR HYDROGEN CHLORIDE, ANHYDROUS

CTC/DOT* Specification Number	Description
3A1800	Seamless steel cylinder. Maximum service pressure 12 400 (1800 psi).
3AA1800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi). Steels definitely prescribed. Maximum carbon content 0.28%.
3E1800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi). Maximum diameter: 51 mm (2 in.). Maximum length: 610 mm (24 in.).
3AX1800	Same as 3A1800 except not less than 450 kg (990 lb.) water capacity.

* Canadian Transport Commission and Department of Transportation (U.S.)

Proceed with off-loading as follows (MCA 1970):

- Before the manhole cover or the discharge outlet is connected, the tank car must be relieved of all internal pressure by slowly loosening bolts on the safety vent flange or alternatively by cooling the outside of the car with water.
- Connect the 51 mm (2 in.) unloading line to the discharge outlet and connect the 25 mm (1 in.) air line. Air pressure must be reduced to 207 kPa (30 psi) for unloading. A safety relief valve must be installed in the air line to release at 242 kPa (35 psi).
- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure in a scrubber system.
- Reverse the above procedure to close up the car.
- For off-loading by pump, the vent cap must remain open to the atmosphere.
- Cars must be depressurized before returning them to the railroad.

The general procedures for unloading hydrochloric acid highway tankers is similar to that of railway tankers.

4.2.2 Off-loading Equipment and Procedures for Hydrogen Chloride Railway Tank Cars. Prior to off-loading hydrogen chloride, anhydrous, measures similar to hydrochloric acid off-loading must be taken.

The railway tank car may be unloaded by vapour pressure or by air padding (MCA 1970). When using the vapour pressure method, liquid hydrogen chloride is discharged from one of the two liquid angle valves. When hydrogen chloride gas is required, the liquid should be vaporized; gas should not be discharged from gas angle valves. During the air padding method, dry air is used to increase car pressure (MCA 1970).

The unloading of hydrogen chloride highway tankers is similar to that of railway tank cars. The general procedures for tank cars apply equally well to tank trailers.

4.2.3 Off-loading Cylinders. The following points should be observed when handling and storing hydrogen chloride, anhydrous, cylinders:

- Valve protection hoods should be in place.
- Cylinders should not be stored near ventilating systems.
- Store to minimize external corrosion.

- Store cylinders upright.
- Store full and empty cylinders separately.

Special control valves and adapters are recommended for connection to the cylinder (MCA 1970). A vacuum break is necessary to prevent "suck back" of a liquid into the cylinder when anhydrous hydrogen chloride is discharged into other liquids.

4.2.4 Specifications and Materials for Off-loading Equipment. The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in hydrogen chloride service. It is recognized that other materials may be used for particular applications, as indicated in Section 4.3.

The materials of construction for the handling and storage of gaseous hydrogen chloride and hydrochloric acid are considerably different and will be discussed separately in this section. Where a specific material-to-equipment relationship is known, it will be highlighted; otherwise, the compatibility discussion will be general (Kirk-Othmer 1980). Specific references may be included.

4.2.4.1 Gaseous hydrogen chloride. Generally, pure hydrogen chloride gas does not react with standard metallic and nonmetallic materials of construction at ambient temperatures. At all but elevated temperatures, the reaction with most metals is slow. The corrosion rate of mild steel, for example, is reported to be 0.25 cm/yr at 300°C; no ignition point has been found at 760°C. The dissociation of the gas at these temperatures is about 10^{-3} percent and 0.2 percent, respectively. Carbon steel can be used with dry hydrogen chloride gas for vessels and pipes up to 250°C and for tubes and internals up to 200°C (CE 1980a).

Water vapour does not influence the corrosion rate of metals as long as no film of adsorbed moisture can form. This condition can be afforded if the temperature is maintained at least 20°C above the dew point of the gas mixture. At atmospheric pressure, a temperature of 130°C or above can be used for all mixtures of hydrogen chloride gas and water vapour, since the azeotropic boiling point is 108.6°C. The azeotropic boiling point data at other pressures is shown below:

Pressure				
kPa	(psi)	Boiling Point (°C)	Density (25°C)	HCl (percent by weight)
6.7	(0.1)	48.724	1.1118	23.42
33	(5.0)	81.205	1.1042	21.883

Pressure		Boiling Point (°C)	Density (25°C)	HCl (percent by weight)
kPa	(psi)			
66	(9.6)	97.578	1.0993	20.916
93	(13.5)	106.424	1.0966	20.360
106	(15.4)	110.007	1.0955	20.155
133	(19.3)	116.185	1.0933	19.734

Oxidizing contaminants (which include oxygen and chlorine) in hydrogen chloride gas, however, can significantly affect the corrosion rate. It should also be noted that iron compounds catalyze the oxidation of hydrogen chloride to chlorine. When such contaminants are present in significant concentrations, the operating temperature in steel equipment should be kept below 316°C, the temperature at which ferric chloride ($FeCl_3$) is vaporized from the metal surface. Also, steel equipment should be pickled to remove mill scale before being put into service because hydrogen chloride gas reacts with metal oxides to form chlorides, oxychlorides and water.

Stainless steel alloys, e.g., 18-8(Cr-Ni), show excellent corrosion resistance to hydrogen chloride gas, moist or dry, to temperatures as high as 400°C; however, they are not usually recommended because they are subject to chloride stress-corrosion cracking during periods of non-use. The latter is especially true for types 304 and 316 (CE 1980a). The corrosion rate of Monel is similar to that of mild steel, whereas pure nickel (99.6 percent Ni) and high-nickel alloys (e.g., Inconel 600) can be used at temperatures up to 525°C. Nickel has good resistance to wet or dry hydrogen chloride gas; however, service with hydrochloric acid is limited. Monel 400, for example, has an upper temperature limit of about 300°C (CE 1980a).

Specifically, anhydrous hydrogen chloride gas and liquid with a moisture content below 150 ppm are commonly handled in steel piping and equipment. Also, nickel-alloy materials, including some low-nickel stainless steels, can be used. Schedule 40 seamless steel pipe, 7.6 cm or larger, in diameter is used for dry gas up to 100 psig and at -26 to 177 °C. Alloy 20 gate, plug and ball valves (rating, 150 psig) are commonly used, as well as Monel valves. Schedule 80 seamless piping (all sizes) with Alloy 20 valves (rating 600 psig) is used for dry liquid hydrogen chloride. Storage tanks for the anhydrous liquid must be constructed of a steel with good low-temperature qualities; carbon steel is satisfactory for most storage temperatures. If hydrogen chloride contains moisture at or above 150 ppm, plastic or rubber lining or special alloys that are suitable for hydrochloric acid must be used for equipment and piping (NAS 1976).

4.2.4.2 Hydrochloric acid. Aqueous hydrochloric acid reacts with most metals according to the equation

$$M + n\,H_3O^+ \rightarrow M^{n+} + n\,H_2O = n/2\,H_2$$

The reaction rate is influenced by the concentration of the acid; the presence of contaminants in the acid that function as oxidizing, reducing or complexing agents; the presence of corrosion inhibitors; the physical form of the metal and the prior history of treatment (annealing, hardening, rolling, etc.); the presence of impurities in the metal; the temperature; the solubility of the chlorides; and the dynamics of the solution (agitation, temperature gradients, etc.).

Carbon steels and cast iron are never used for hydrochloric acid service. Addition of other metals to iron usually increases iron's resistance to the acid, e.g., high silicon cast iron will handle all acid concentrations up to 93°C. The latter, however, is not suitable for boiling concentrated solutions or ones containing oxidizing salts such as ferric or cupric chloride. Other alloys containing nickel, chromium, molybdenum, copper, manganese, tungsten and antimony have been evaluated. Generally, stainless steels perform less than satisfactorily; however, a Japanese stainless steel (16-18Ni, 9-11Cr, 6-8Mo, 2Mn, 1Si, 0.04P) is reported to have good resistance to hot hydrochloric acid.

Pure molybdenum and tungsten are very resistant to hydrochloric acid at room temperature and to 10 percent concentration at 100°C. Their resistance is unacceptable to boiling 20 percent acid. Both tantalum and zirconium are quite resistant to concentrations up to 40 percent and temperatures up to 100°C. Corrosion rates for both are reported to be less than 50 μm per year. The presence of ferric or cupric chlorides seriously impairs the resistance of zirconium. Tantalum-molybdenum alloys with more than 50 percent of the former have excellent corrosion resistance.

Nickel-based alloys have corrosion resistance superior to that of iron-based alloys. However, nickel-molybdenum alloys containing 60-70 percent nickel and 25-33 percent molybdenum are the only alloys recommended for hot concentrated hydrochloric acid. Both Chlorimet 2 (63Ni, 32Mo, 3Fe) and Hastelloy B (60Ni, 28Mo, 6Fe) show good results with all acid concentrations in the absence of air and iron chlorides.

Other metals or alloys with resistance to hydrochloric acid solutions are lead and electrolysis nickel (2-10P). The former has been used in fully supported piping and as a lining material. It is usable for up to 30 percent acid with some corrosion and up to

20 percent acid at the boiling point. One of the main problems is that lead chloride is moderately soluble in hydrochloric acid. Addition of 6-15 percent antimony increases lead's corrosion resistance. Air and ferric chloride accelerate the corrosion of lead. Other detrimental properties of lead are its high coefficient of thermal expansion and its limited mechanical strength. Durichlor (14.5Si, 3Mo, 82Fe) shows excellent resistance to hot hydrochloric acid in the absence of ferric chloride.

Both carbon and impervious graphite are among the most important materials for hydrochloric acid service. The graphite is usually impregnated with 10-15 percent of a phenolic, epoxy or furan resin to make it impervious. The latter imposes a maximum temperature limit of 170°C. These materials are generally used as heat exchange or centrifugal pump materials. Glass is widely used as a lining; it is sometimes used in all-glass equipment and components such as piping and pumps. The corrosion resistance varies with the type of glass. Fused-cast refractories (alumina, silica, zirconia and chrome alumina) are also used as lining materials. Monolithic refractories are satisfactory for applications such as stoneware vessels.

Generally, the commonly used plastics and elastomers show excellent resistance to hydrochloric acid within the temperature limits of the specific material. Soft natural rubber compounds are excellent as liner materials for storage tanks at temperatures up to 60°C. Semihard rubber compounds are used as linings in pipes and equipment up to 70°C. Hard rubber is used for pipes up to 50°C and pressures up to 446 kPa. Organic contaminants in the acid make it necessary to use neoprene, nitrile, butyl, chlorobutyl, hypalon and EPDM elastomers in place of natural rubber. Plastics such as polypropylene, polyvinylchloride, Saran and ABS show good resistance. Fluorocarbon plastics also have extremely high corrosion resistance and a high upper temperature limit.

Some temperature limits and materials are shown below (Dow 1979):

Material	Recommended Temperature Ranges
PTFE	-29 to 260°C
Kynar (PVDF)	-18 to 135°C
Polypropylene	-18 to 107°C
Saran	-18 to 80°C

4.3 Compatibility with Materials of Construction

The compatibility of hydrochloric acid with materials of construction is indicated in Table 8. The unbracketed abbreviations are described in Table 9. The rating system for this report is briefly described below.

Recommended:	This material will perform satisfactorily in the given application.
Conditional:	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
Not Recommended:	Material will be severely affected in this application and should not be used.

TABLE 8 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and[1] Fittings	25-40%	23	PVC II (DPPED 1967)		
	≈ (conc.) 36%	50	NR (hard) (Kirk-Othmer 1980)		
	25-40%	60		PVC II (DPPED 1967)	
	<35%	To operating limit of material	PVC I* ABS*, PE* (MWPP 1978)		
	35%	200	PTFE (Dow 1979)		
	35%	204	Teflon, FEP (CE 1981)		
	35%	135	PVDF (DCRG 1978)		
	35%	121	Chlorinated Polyether (DCRG 1978)		
	≈ (conc.) 36%	70	NR(semihard) (Kirk-Othmer 1980)		
	35%	79	PVDC (DCRG 1978)		
	38%	52	PP (CE 1980b)		
2. Valves	All concentrations	21			SS 316 "20" Alloy (JSSV 1979)
	Up to 37%	90	Cer-Vit C126 (Schott)		

TABLE 8 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
2. Valves (cont'd)	100% gas, dry	-26 to 177	Alloy 20 (NAS 1976)		
	100% liq., dry	-	Alloy 20 (NAS 1976)		
3. Pumps	Comme[illegible] Conc.	93	High Silicone Cast Iron (HIS 1969)		
4. Storage	100%, dry liq.	-	CS Steel (with good low temp. qualities) (NAS 1976)		
	100%, dry gas	65.5	FGR (Smith 1982)		
	100% gas, wet or dry	>130 ≤250	CS (CE 1980a; Kirk-Othmer 1980)	SS 304, 316 (CE 1980a)	
	100% gas, wet or dry	>130 ≤300	Monel 400 (CE 1980a)		
	100% gas, wet or dry	>130 ≤400	SS 18-8 Cr-Ni (CE 1980a)		
	100% gas, wet or dry	>130 ≤500	Ni, Inconel 600 (CE 1980a; Kirk-Othmer 1980)		
	100% gas, dry	-26 to 177	Steel (Scd 40) (NAS 1976)		
	100% liq., dry	-	Steel (Scd 80) (NAS 1976)		
5. Others	20	79	PP (CE 1980b)		
	Up to 30%	40	uPVC PE PP CR CSM (GF)	IIR EPDM FPM (GF)	POM NR NBR (GF)

TABLE 8 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (cont'd)	Up to 30%	60	PE PP CR CSM (GF)	uPVC IIR EPDM FPM (GF)	POM NR NBR (GF)
	>30%	20	uPVC PE PP CSM (GF)	IIR EPDM CR FPM (GF)	POM NR NBR (GF)
	>30%	60	uPVC PP CSM (GF)	PE CR (GF)	POM NR NBR IIR EPDM (GF)
	>30%	80	CSM (GF)	CR** (GF)	uPVC PE PP POM NR NBR IIR EPDM FPM (GF)
	38%		IIR** CM EPDM** (GPP)		SBR CR (GPP)
	>10%	All temp.			SS 302 SS 304 SS 316 SS 410 SS 430 (ASS)
	38%	60	PVC (TPS 1978)		
	38%	85	NR (hard) (CE 1980b)		
	38%	100	CPVC (TPS 1978)		
	38%	52	PP (CE 1980b)		

TABLE 8 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

	Chemical		Material of Construction		
Application	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (cont'd)	38%	134	PVDF (CE 1980b)		
	90%	24	Glass (CDS 1967)		
	100%	-			SS 304 SS 316 (CE 1980a)
	100%	24-100	Glass (CDS 1967)		
	100%	24	Wood (CDS 1967)		Concrete (CDS 1967)
	100%	200	TFE (CE 1980b)		
	100%	204	FEP (CE 1980b)		
	up to 5%	70		Monel 400 (CE 1980a)	
	up to 10%	RT	Ni, Monel 400 (CE 1980a)		
	up to 20%	RT		Ni, Monel 400 (CE 1980a)	
	up to 38%	RT	Hastelloy C-4 Inconel 825 (CE 1980a)		
	up to 20%	108	Hastelloy B-2 Zr Ta (CE 1980a)		
	up to 30%	92	Hastelloy B-2 Zr Ta (CE 1980a)		
	up to 38%	59	Hastelloy B-2 Zr Ta (CE 1980a)		
	all conc.	-	Glass[2] (Kirk-Othmer 1980)		

TABLE 8 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others (cont'd)	all conc.	38		Nb (CE 1983)	
	all conc.	38			Ti (CE 1983)
	all conc.	38	Hastelloy C-276 (CE 1983)		
	all conc.	38			Carpenter Alloy (CE 1983)
	10%	102	KBI-40 (CE 1983)		
	20%	110	KBI-40 (CE 1983)		KBI-40 = 60% Ta, 40% Nb
	30%	92	KBI-40 (CE 1983)		
	36%	81	KBI-40 (CE 1983)		
	5%	25	Ti (AMC)		
	10%	35		Ti (AMC)	
	10%	25			Nylon (C-I-L 1982)
	2.5%	23	Nylon (C-I-L 1982)		
	all conc.	60	NR (soft) (Kirk-Othmer 1980)		
	all conc.	170	Graphite^3 (Kirk-Othmer 1980)		
	38%	100	Graphite, impervious (CE 1980b)		
	10%	93	FGR (Polythread) (Smith 1982)		
		65.5	FGR (Green Thread) (Smith 1982)		
			FGR (Chemline) (Smith 1982)		

TABLE 8 COMPATIBILITY WITH COMMON MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical Conc.	Chemical Temp. (°C)	Material of Construction: Recommended	Conditional	Not Recommended
5. Others (cont'd)	20%	93	FGR (Polythread) (Smith 1982)		
		65.5	FGR (Greenthread) (Smith 1982)		
			FGR (Chem-line) (Smith 1982)		
	36.5%	65.5	FGR (Polythread) (Smith 1982)		
		24	FGR (Green Thread) (Smith 1982)		

Chemical	Operating Temperature (°C)	Chemical Resistance Min.	Chemical Resistance Acids
PE			
Low ρ	60-77	G	
Med ρ	71-93	E	weak & strong
Hi ρ	92-200	E	
PVC			
Rigid	70-74	weak - E; strong - G to E	
Nonrigid	80-105	weak - F to G; strong - F to G	
ABS	88-110	G - weak and strong	

(CRC 1982)

** This material has been given a lower rating in a similar application by another reference.

1 The materials shown for use with hydrochloric acid are generally considered as lining materials for piping. The listing is not all-inclusive. Other materials that may have application for piping under normal special conditions are listed under "Other".

2 Corrosion resistance varies with type of glass.

3 Impregnated with epoxy, phenolic or furan resins.

TABLE 9 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Alloy 20 (super stainless steel, 20.22% Cr, 25-46% Ni, 2-6.5% Mo)
	Cast Iron, High Silicone
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene) Rubber
CS	Carbon Steel
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Concrete
EPDM	Ethylene Propylene Rubber
FGR	Fibreglass Reinforced Systems
FPM	Fluorine Rubber (Viton)
	Glass
	Hastelloy
IIR	Isobutylene/Isoprene (Butyl) Rubber
	Inconel
	Nickel
KBI-40	60% Tantalum, 40% Niobium
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) rubber
NR	Natural Rubber
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (Followed by grade, if any)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride
SBR	Styrene/Butadiene (GR-5, Buna S) Rubber
SS (Followed by grade)	Stainless Steel
Ta	Tantalum

TABLE 9 MATERIALS OF CONSTRUCTION (Cont'd)

Abbreviation	Material of Construction
TFE, FEP, PTFE	Teflon
Ti	Titanium
uPVC	Unplasticized Polyvinyl Chloride
	Wood
Zr	Zirconium

5 CONTAMINANT TRANSPORT

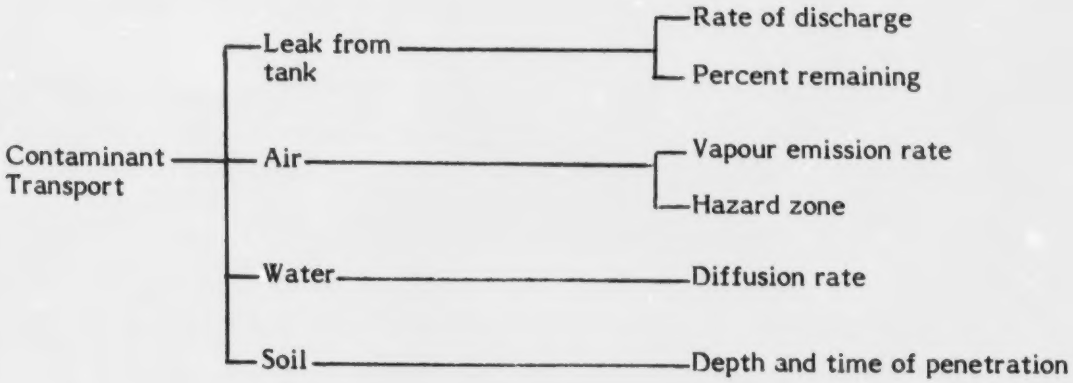
5.1 General Summary

Anhydrous hydrogen chloride is commonly transported under pressure as a liquid while hydrochloric acid is transported in unpressurized tank cars. When spilled in the environment, both will form liquid pools, spreading on the surface of the ground, and a vapour cloud. Vapour is released from the pool to the atmosphere by evaporation, rapidly in the case of anhydrous hydrogen chloride (in the form of a puff) and less rapidly in the case of hydrochloric acid.

When spilled on water, hydrogen chloride/hydrochloric acid will sink and dissolve rapidly. A spill of the former will boil and rapidly release vapour. Both liquids will also dissolve in water to a large extent.

Hydrogen chloride and hydrochloric acid spills on soil surfaces will partly vaporize, and partly be adsorbed onto the soil at a rate dependent on the soil type and its degree of saturation with water. Downward transport of the liquid toward the groundwater table may be an environmental concern. Only a limited portion of the anhydrous product will penetrate because of its rapid vaporization. Both the acid and the anhydrous product will rapidly mix with any available water and thus continue penetration as a more dilute solution.

The following factors are considered for the transport of spill in the air, water and soil media:


Contaminant Transport
Leak from tank
Rate of discharge
Percent remaining
Air
Vapour emission rate
Hazard zone
Water
Diffusion rate
Soil
Depth and time of penetration

It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Hydrochloric acid, aqueous, is commonly transported in unpressurized tank cars at a maximum 38 percent solution. Alternatively, anhydrous hydrogen chloride may be transported under pressure as a liquid. While the capacities of railway tank cars vary widely, one size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L. Leak nomograms have been prepared for both the non-pressurized aqueous solution (hydrochloric acid) and the pressurized anhydrous form (hydrogen chloride).

5.2.2 Leak Nomograms - Hydrochloric Acid (Aqueous). If a tank car loaded with hydrochloric acid is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the venting rate of the liquid. Because of the relatively low volatility of hydrochloric acid, and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

The rate of outflow (q) from a puncture hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the fluid above the puncture hole (H), and a coefficient of discharge (C_d).

As the gravitational force predominates over viscous and other forces for a wide range of fluid conditions, the rate of discharge is relatively independent of fluid temperature and viscosity (Rouse 1961).

5.2.2.1 Figure 11: Percent remaining versus time. Figure 11 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of hydrochloric acid. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

FIGURE 11

HYDROCHLORIC ACID

PERCENT REMAINING VS TIME

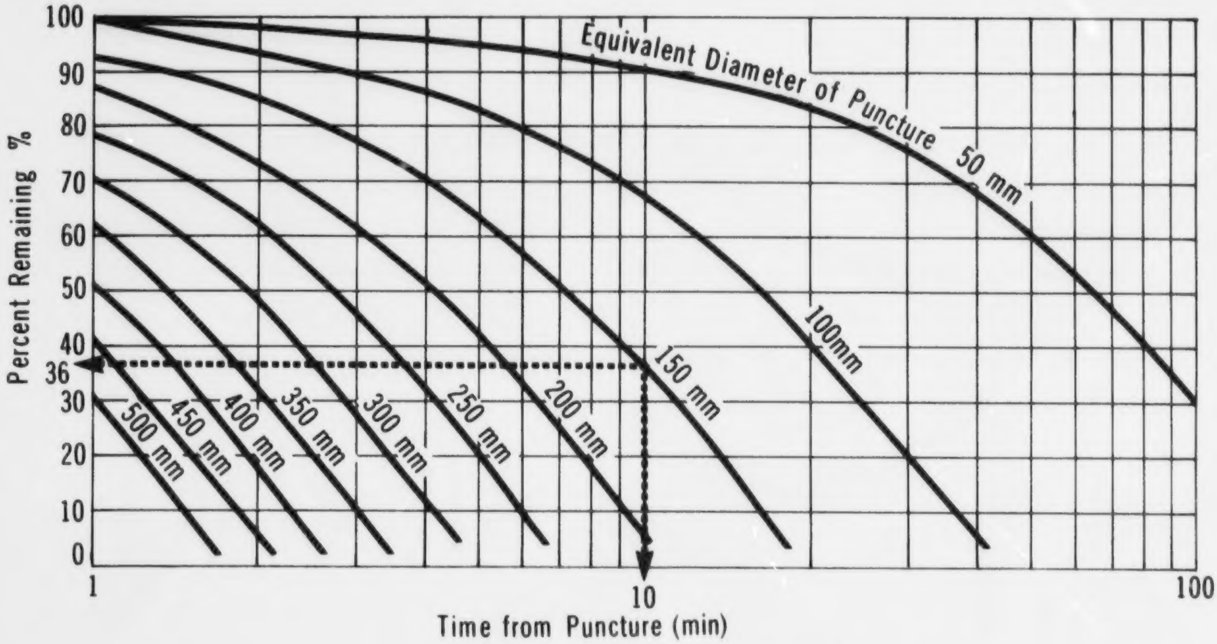
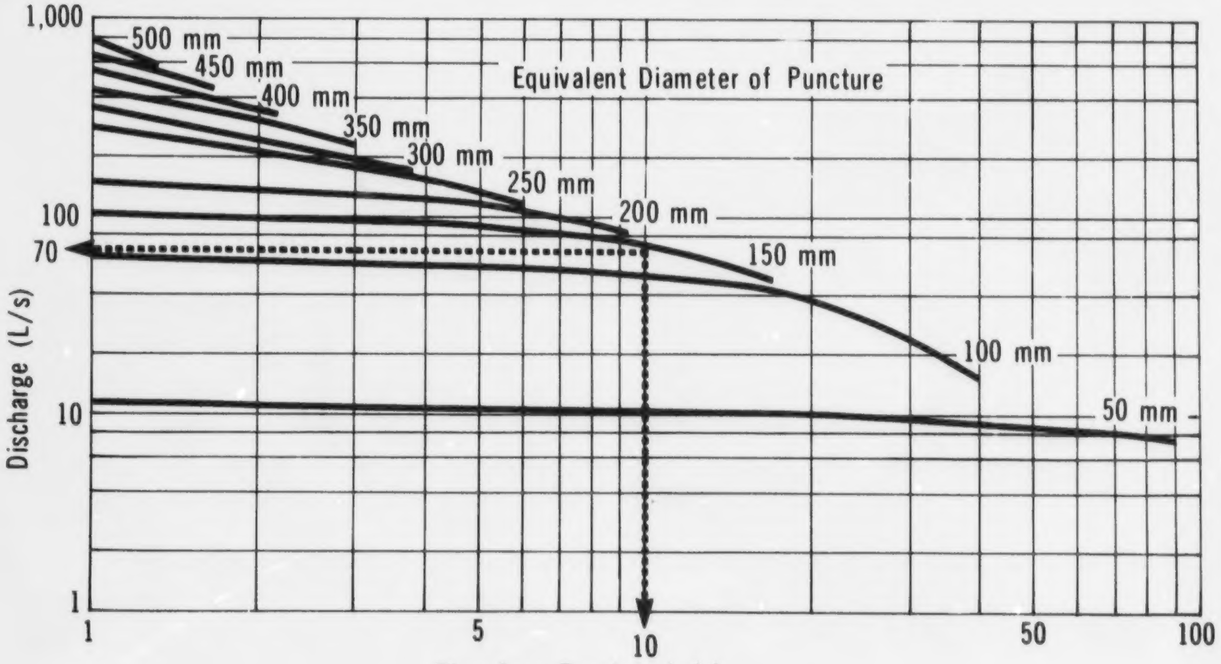


FIGURE 12

HYDROCHLORIC ACID

DISCHARGE RATE VS TIME



5.2.2.2 **Figure 12: Discharge rate versus time.** Figure 12 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of puncture, for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80 000 L.

5.2.3 **Leak Nomograms - Hydrogen Chloride (Anhydrous).** If a tank car loaded with hydrogen chloride is punctured on the bottom, all of the contents will drain out. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole size (A) and shape, and a coefficient of discharge (C_d).

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal), equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. In reality, however, the evaporation of the gas will cause cooling of the liquid and a decrease in the evaporation rate. This cooling may also (in some spill circumstances) cause water ice to form at the liquid surface, thus further reducing the evaporation rate. The assumption of isothermal conditions thus presents the fastest release rate and therefore worst-case conditions.

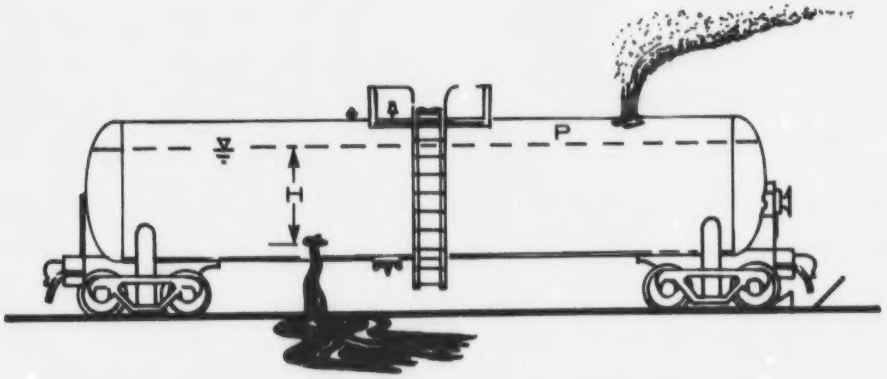


FIGURE 13 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

The aim of the nomograms is to provide a simple means to obtain the time history of the venting process. This may include venting from a bottom puncture (liquid release) or from a puncture above the liquid level (gas venting). The details of the models used to calculate venting rates are described in the Introduction Manual.

5.2.3.1 Bottom puncture - liquid venting.

Figure 14: Percent remaining versus time. Figure 14 provides a means of estimating the percent of hydrogen chloride remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The tank car is assumed to be initially full (at t=o) with a volume of about 80 000 L of hydrogen chloride at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 15: Discharge rate versus puncture size. Figure 15 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.3.2 Top puncture - gas venting.

Figure 16: Percent remaining versus time. Figure 16 provides a means of estimating the percent of hydrogen chloride remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

As isothermal conditions have been assumed, the internal pressure and venting rate are presumed to be constant. In actual spill circumstances, it has been noted that 25 to 30 percent may flash off rapidly and the remainder, because of evaporative cooling, may be much slower than predicted here.

Figure 17: Discharge rate versus puncture size. Figure 17 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

The values presented in Figure 17 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 600 kPa.

FIGURE 14

HYDROGEN CHLORIDE

PERCENT REMAINING vs TIME

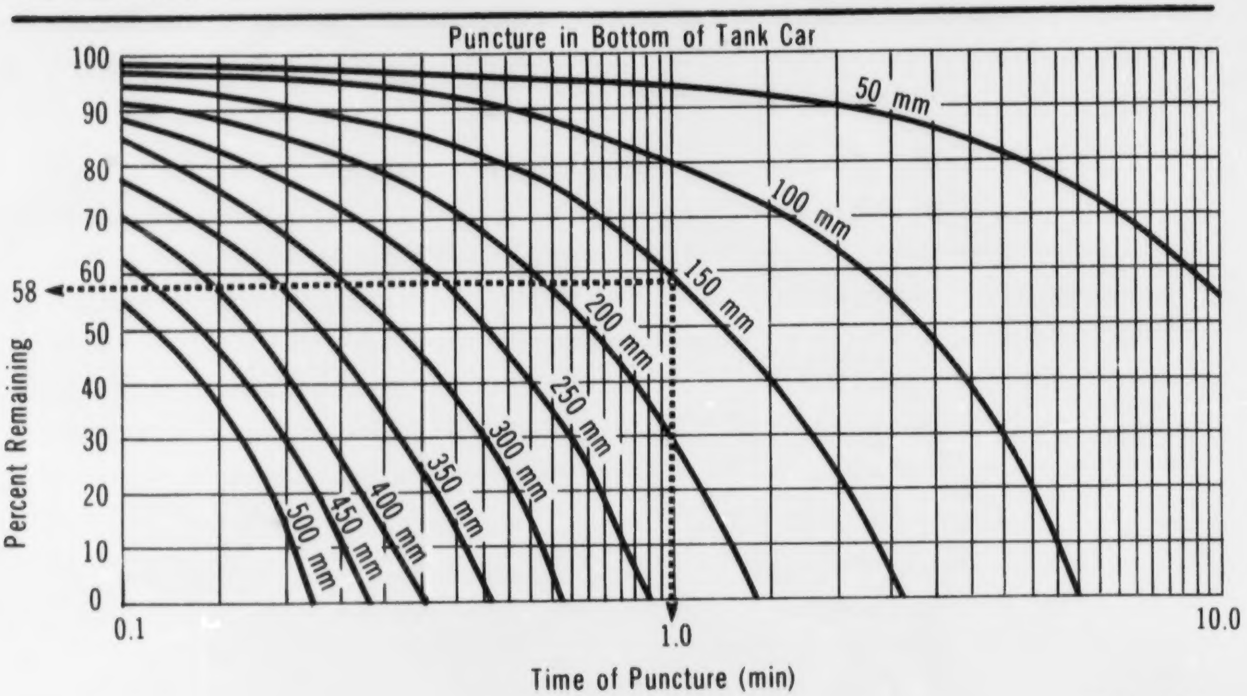


FIGURE 15

HYDROGEN CHLORIDE

DISCHARGE RATE vs PUNCTURE SIZE

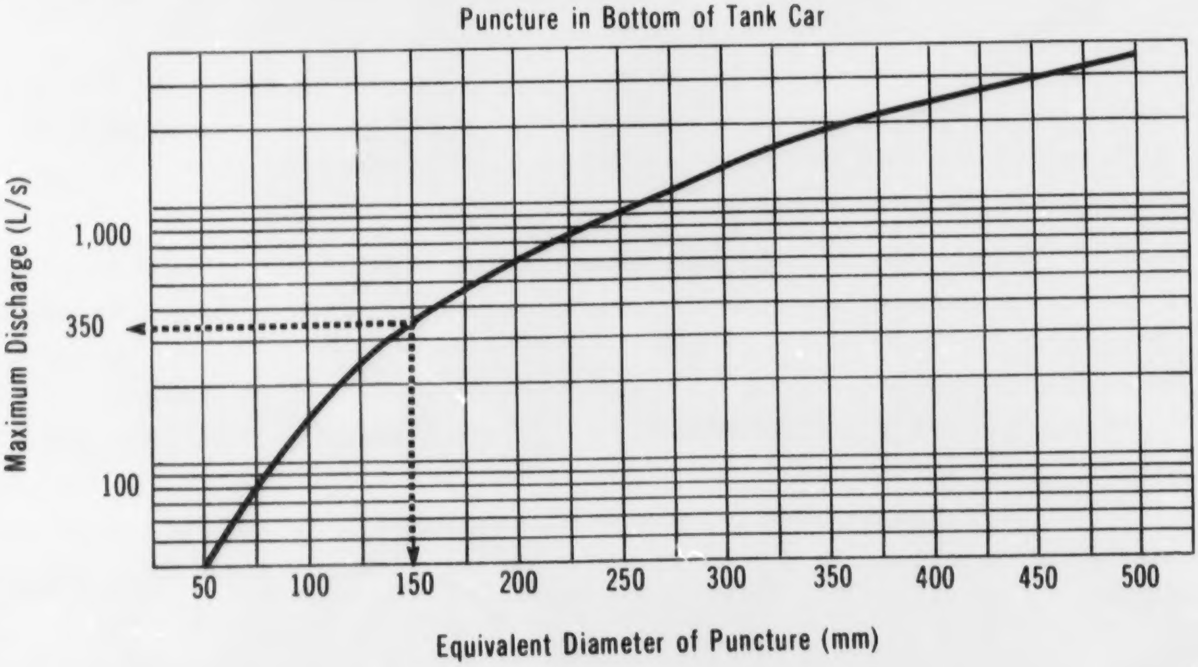


FIGURE 16

HYDROGEN CHLORIDE

PERCENT REMAINING vs TIME

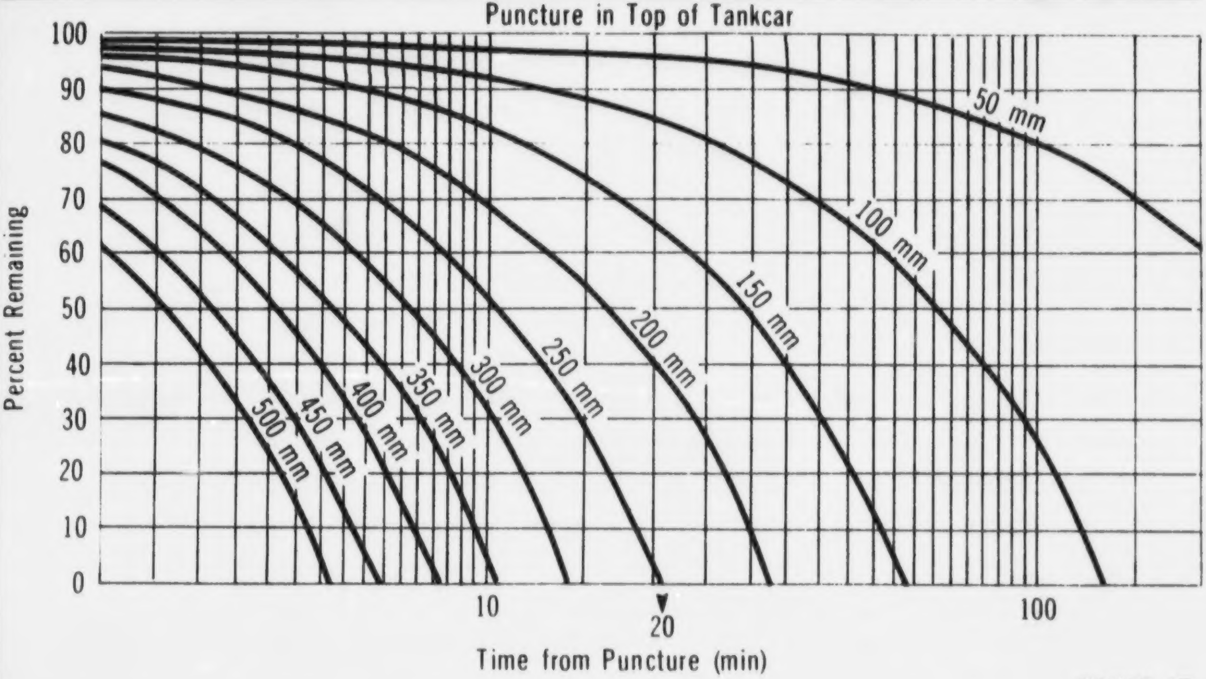
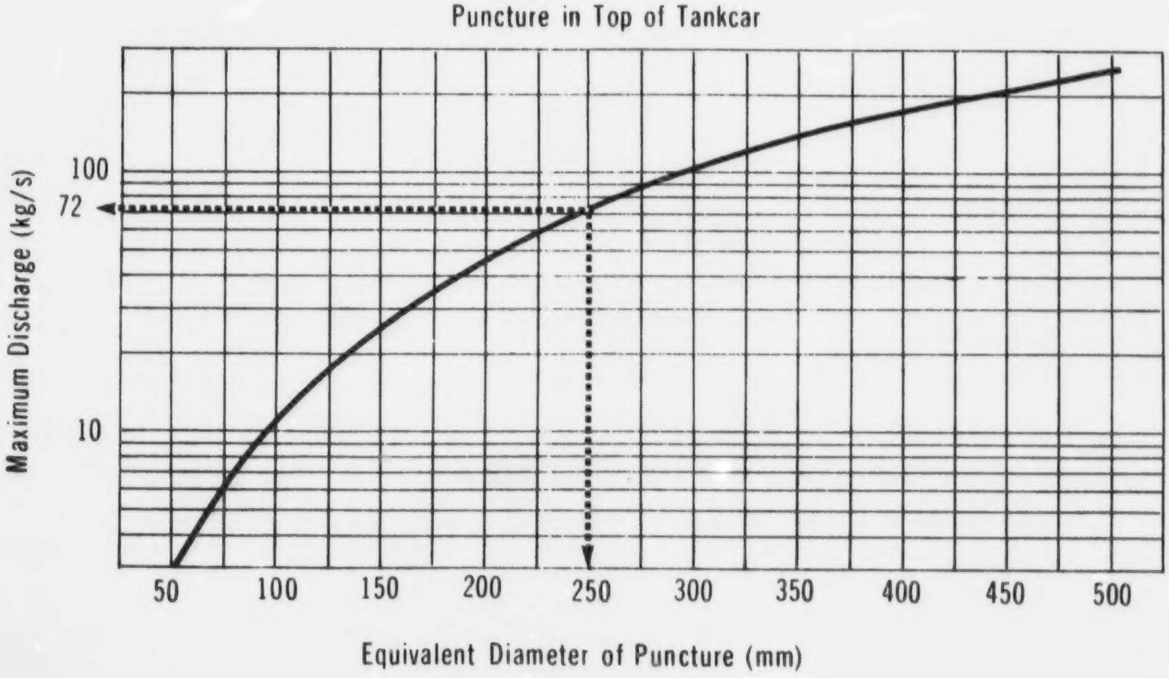


FIGURE 17

HYDROGEN CHLORIDE

DISCHARGE RATE vs PUNCTURE SIZE



5.2.4 Sample Calculations.

i) Problem A

The standard tank car filled with hydrochloric acid, aqueous, has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 11
- With t=10 min and d=150 mm, about 28 000 L, or 36 percent, remain

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

- Use Figure 12
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

iii) Problem C

The standard tank car filled with anhydrous hydrogen chloride at 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 1 minute and what is the instantaneous discharge rate from the tank?

Solution to Problem C

Step 1: Calculate amount remaining at t=1 min

- Use Figure 14
- With t=1 min and d=150 mm, the amount remaining is about 58 percent or 46 000 L

Step 2: Calculate the discharge rate

- Use Figure 15
- With d=150 mm, the instantaneous discharge rate (q) = 350 L/s

iv) Problem D

The Standard tank car in Problem C has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate, assuming isothermal conditions?

Solution to Problem D

Step 1: Calculate the time to empty

- Use Figure 16
- With d=250 mm, the tank empties (0 percent remaining) in approximately 20 min

Step 2: Calculate the discharge rate

- Use Figure 17
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 72 kg/s

5.3 Dispersion in the Air

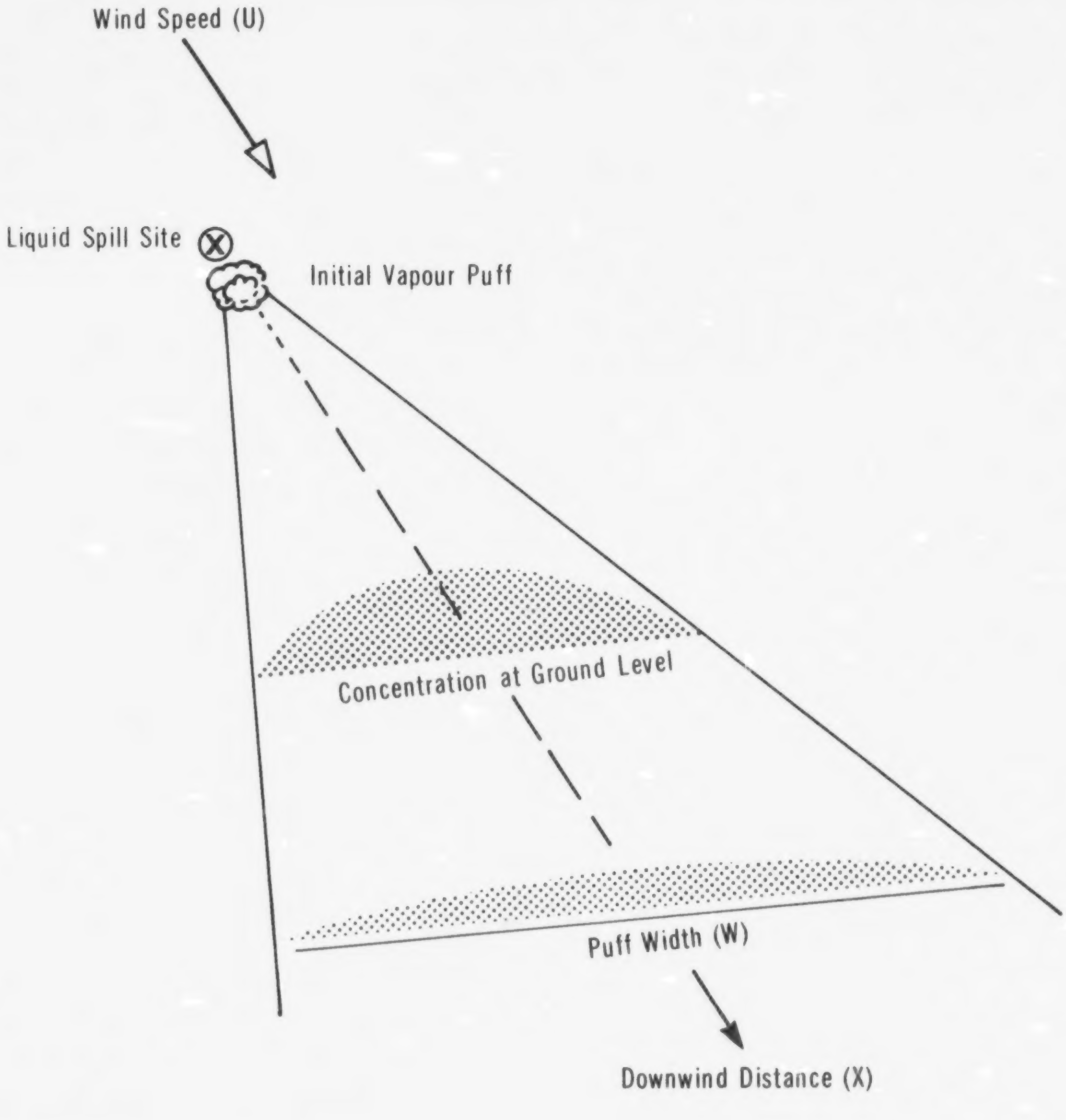
5.3.1 Introduction. Since hydrogen chloride under pressure is an extremely volatile liquid, vapour from a liquid pool on a ground or water surface is released rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Only this type of vapour release is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 18 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

Although no relevant spill information is available on the behaviour of a cloud of hydrogen chloride gas, it is expected that in the initial period immediately after the spill, the cloud will behave as a denser-than-air gas. This is due primarily to the greater density of hydrogen chloride gas (1.3 times that of air at 20°C) and to the fact that the vapour cloud arising from the cold bulk liquid will itself be cold. Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussian modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed. The vapour cloud will also begin to react with atmospheric moisture immediately after release, forming a cloud of hydrochloric acid. This phenomenon will be very rapid in locations with high humidity.

SCHEMATIC OF CONTAMINANT PUFF


Wind Speed (U)
Liquid Spill Site
Initial Vapour Puff
Concentration at Ground Level
Puff Width (W)
Downwind Distance (X)

Spills of hydrochloric acid may be treated in the same manner as spills of anhydrous hydrogen chloride. Since hydrochloric acid is less volatile than anhydrous hydrogen chloride, the use of the vapour dispersion nomograms and tables presented for anhydrous hydrogen chloride will overestimate the hazard resulting from hydrochloric acid spills.

5.3.2 **Vapour Dispersion Nomograms and Tables.** The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Table 10:	weather conditions
Figure 20:	normalized vapour concentration as a function of downwind distance and weather conditions
Table 11:	maximum puff hazard half-widths
Figure 22:	vapour puff travel distance as a function of time elapsed since the spill and wind speed

The flow chart given in Figure 19 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

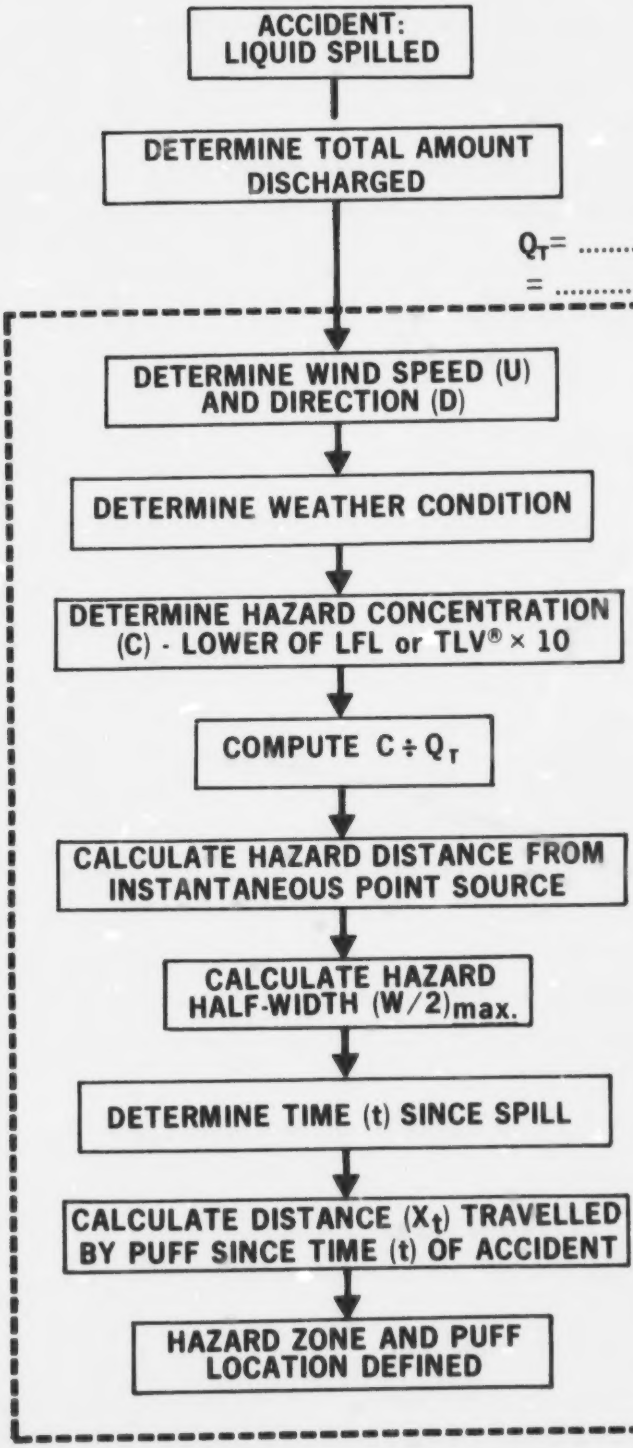
5.3.2.1 **Figure 20: Vapour concentration versus downwind distance.** Figure 20 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 19, the weather condition must be determined from Table 10.

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 20 knowing:

- Q_T, the mass of vapour emitted (equivalent to liquid spilled)
- U, the wind speed (m/s)
- the weather condition

FIGURE 19

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE


ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE $C \div Q_T$
CALCULATE HAZARD DISTANCE FROM INSTANTANEOUS POINT SOURCE
CALCULATE HAZARD HALF-WIDTH $(W/2)_{max.}$
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (X_t) TRAVELLED BY PUFF SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PUFF LOCATION DEFINED

Step 1: Use Figure 16 Section 5.2

Time since puncture........ minutes

Equivalent diameter of puncture .... mm

Percent of chemical remaining .... %

Amount discharged:

q = 80,000 L − % × 80,000 L = ... L

Q_T= .... L × density (kg/L) ÷ 1000 = ... tonnes

= .... tonnes × 10^6 grams/tonne = ... grams

Step 2: Observed or estimated

U = ... km/h; D = ... degrees

Step 3: Use Table 10

Condition = ...

Step 4: C = 0.07 g/m³ for Hydrogen Chloride 10 × TLV® (1981)

Step 5: Computation required

C/Q_T = ... m^{-3}

Step 6: Use Figure 20

X = ... km

Step 7: Use Table 11

$(W/2)_{max.}$ = ... m

Step 8:

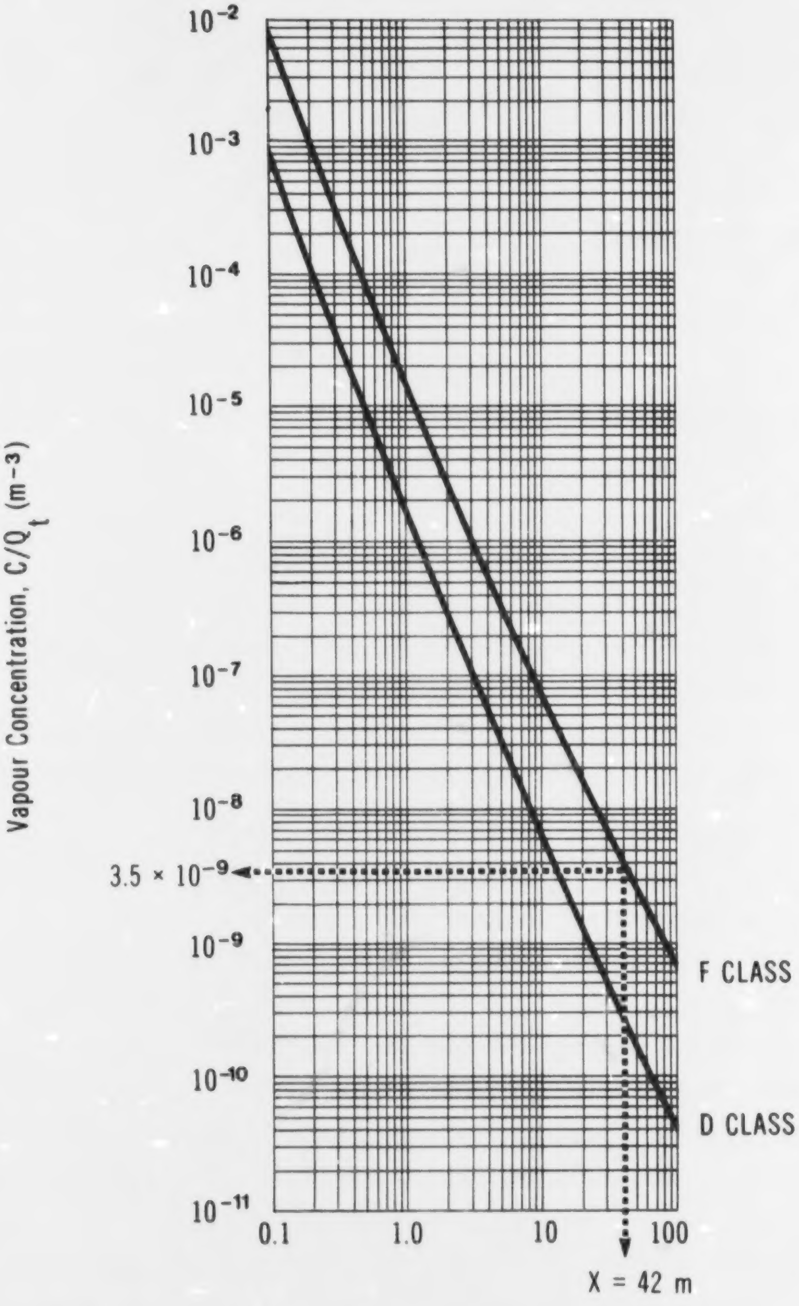
t = ... s

Step 9: Use Figure 22 with U from Step 2

X_t = ... km

FIGURE 20

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



Maximum Downwind Hazard Distance, X (km)

TABLE 10 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed less than 11 km/h (≈ 3 m/s) one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

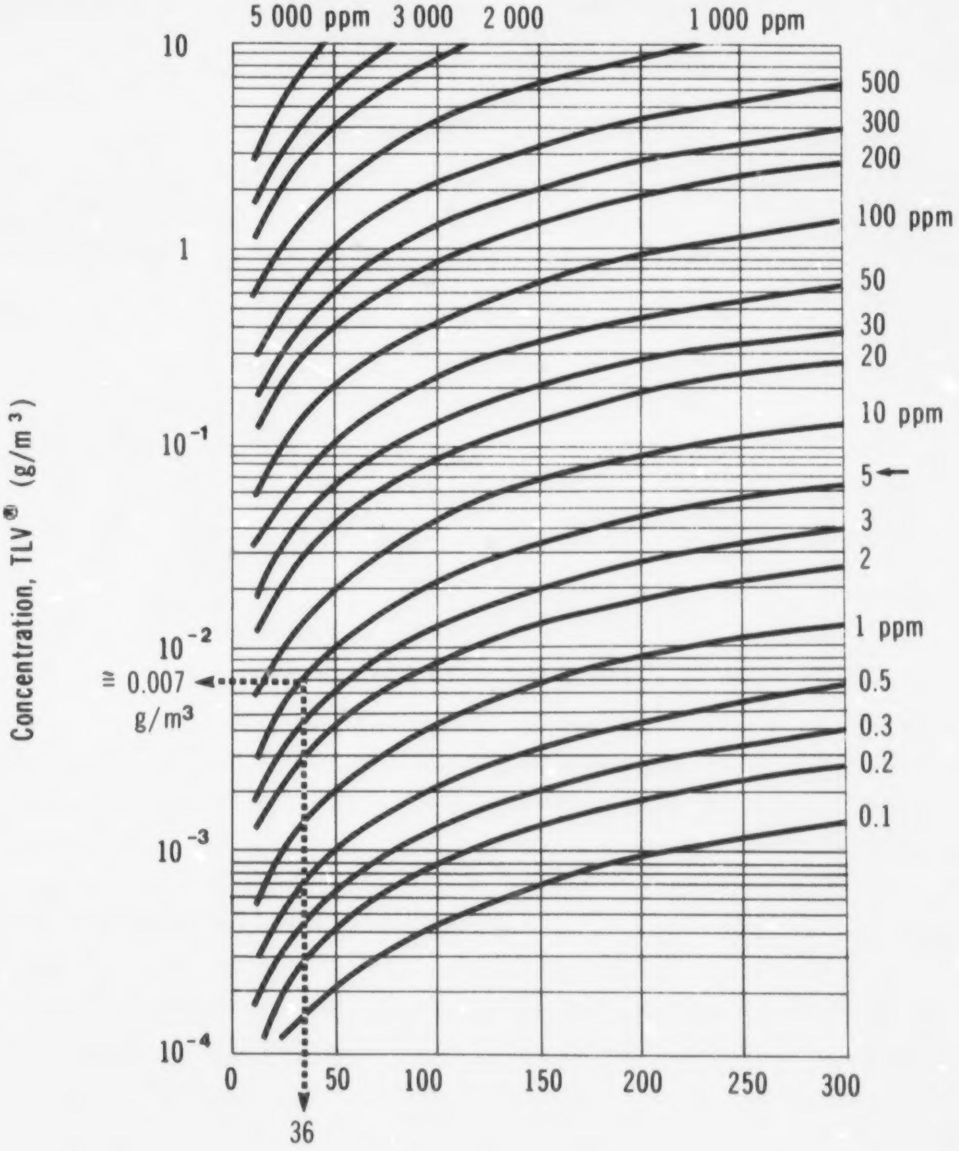
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value® (TLV, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3), which for an inflammable vapour will be 10 x TLV®. Note: To convert the TLV®, in ppm, to a concentration in g/m^3, use Figure 21.

A hazard concentration limit of 10 times the TLV® has been chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones. It should be noted that the level of 50 ppm has shown health effects in humans as noted in Chapter 7 of this report. It should also be noted that 5 ppm is a "ceiling" limit for the workplace and no short-term exposure limits have been developed.

5.3.2.2 **Table 11: Maximum puff hazard half-widths.** This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the hydrogen chloride Threshold Limit Value (TLV®) of 0.007 g/m^3, or 0.07 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the hydrogen chloride vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 11 is therefore only applicable for a hydrogen chloride hazard concentration limit of 10 x TLV®, or 0.07 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 2250 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Molecular Weight

Example: Hydrogen Chloride, MW = 36, TLV® = 5 ppm, then TLV® in g/m³ ≅ 0.007

Note: data applicable at 25° and 760 mm Hg pressure

TABLE 11 MAXIMUM PUFF HAZARD HALF-WIDTHS (for hydrogen chloride)

Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)	
2 250	4 030	(99.4 km)*	100	1 825	(97.1 km)*
2 000	3 850		75	1 610	
1 500	3 450		50	1 360	
1 000	2 950		25	1 010	
750	2 650	Q_T=20 tonnes →	20	915	→$(W/2)_{max}$ = 915 m
500	2 265		10	680	
400	2 080		7.5	600	
300	1 860		5	505	
200	1 600		2	350	
100	1 225		1	270	
75	1 010		0.75	240	
50	940		0.50	205	
25	720		0.20	145	
20	670		0.10	110	
10	520		0.075	100	
7.5	465		0.05	85	
5	400		0.01	45	
2	285				
1	220				
0.75	200				
0.50	170				
0.20	120				
0.1	95				
0.075	85				
0.05	75				
0.01	40				

* Data are provided up to a maximum downwind hazard distance of 100 km

Example: Under weather condition F and Q_T = 20 tonnes, the puff hazard half-width $(W/2)_{max}$ = 915 m

Note: Above table is valid only for a hydrogen chloride concentration of 10 x TLV®, or 0.07 g/m^3.

mass spilled would be 95 200 kg, or approximately 95 tonnes. Therefore, under class D of Table 11, data are provided for up to 23 times this amount to allow for the modelling of large incidents.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 0.01 to 100 tonnes, respectively. Therefore, under class F of Table 11, data are provided for up to one 30 000 L tank.

Use: Knowing the weather condition and Q_T, pick the closest value in the table and the corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For an intermediate value, interpolate Q_T and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 11.

5.3.2.3 **Figure 22: Puff travel time versus travel distance.** Figure 22 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t), which indicates how far downwind the puff has travelled, can be determined.

5.3.3 **Sample Calculation.** The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid hydrogen chloride. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

Problem

During the night, at about 2:00 a.m., 20 tonnes of anhydrous hydrogen chloride were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

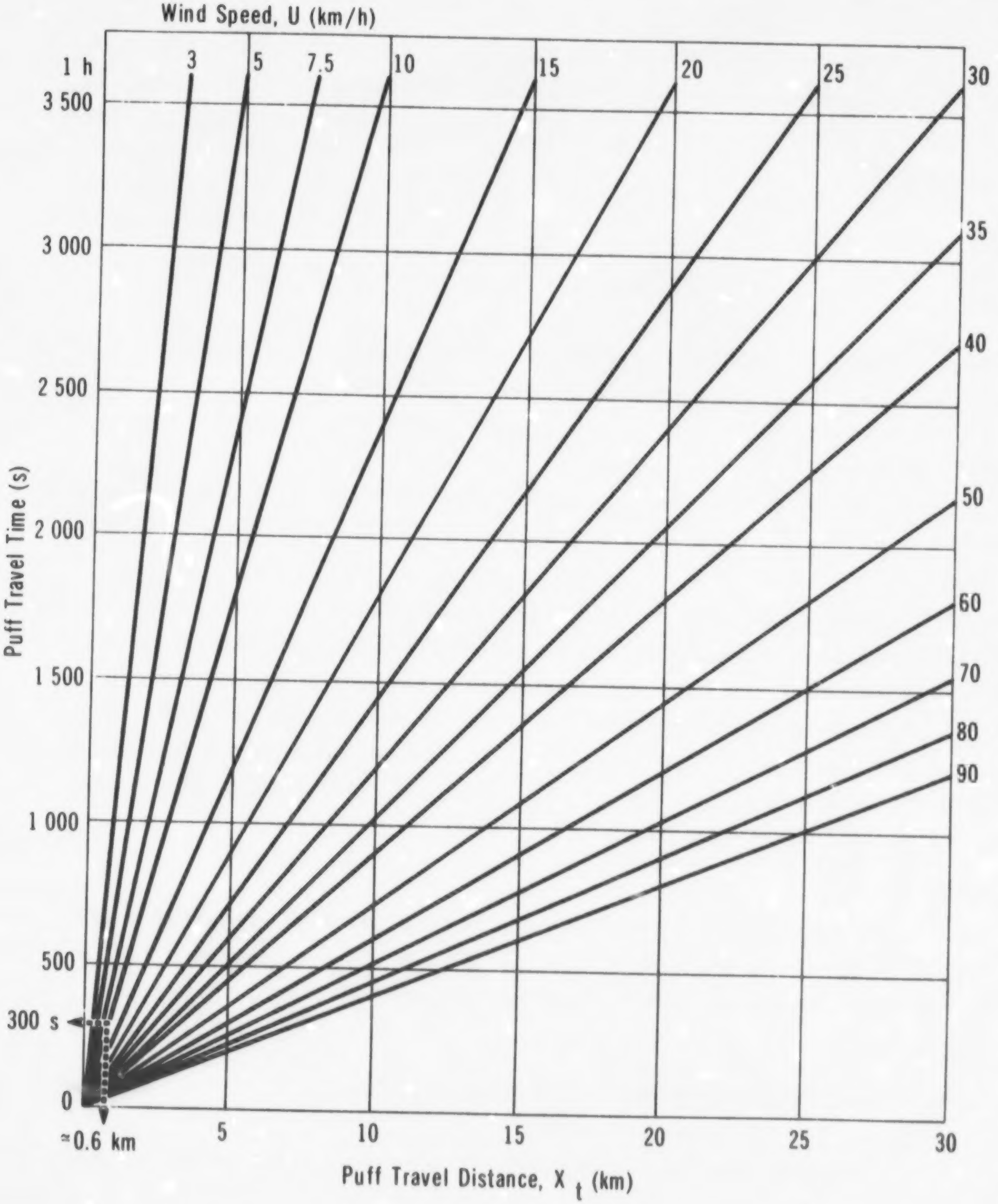
Solution

Step 1: Quantity spilled is given, Q_T = 20 tonnes

- Q_T = 20 tonnes or 20×10^6 g
- $Q_T = 2 \times 10^7$ g

FIGURE 22

PUFF TRAVEL TIME VS TRAVEL DISTANCE



Step 2: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given: $U = 7.5$ km/h, then $U = 7.5 \div 3.6 = 2.1$ m/s
  D = NW or 315° (D = Direction from which wind is blowing)

Step 3: Determine the weather condition

- From Table 10, weather condition = F since U is less than 11 km/h and it is night

Step 4: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL; since hydrogen chloride vapours are not flammable, this is 10 x TLV®
  $C = 0.07\ g/m^3$ (TLV® = $0.007\ g/m^3$; no LFL)

Step 5: Compute C/Q_T

- $C/Q_T = \frac{0.07}{2 \times 10^7} = 3.5 \times 10^{-9}\ m^{-3}$

Step 6: Calculate the puff hazard distance (X) from the instantaneous point source

- From Figure 20, with $C/Q_T = 3.5 \times 10^{-9}\ m^{-3}$ and weather condition F, $X \approx 42$ km

Step 7: Calculate the puff hazard half-width $(W/2)_{max}$

- Use Table 11
- With $Q_T = 20$ tonnes
- Then for weather condition F, $(W/2)_{max} = 915$ m

Step 8: Determine the time since spill

- $t = 5\ min \times 60 = 300$ s

Step 9: Calculate the distance travelled (X_t) by the vapour puff since the time of the accident

- Using Figure 22, with $t = 300$ s and $U = 7.5$ km/h, then $X_t = 0.6$ km (more accurately from $X_t = Ut = 2.1\ m/s \times 300\ s = 630\ m = 0.63$ km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (915 m) by the maximum hazard distance downwind of the instantaneous point source (42 km) along the direction of the wind, as shown in Figure 23

- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 24
- Note that the puff has only travelled 0.63 km in the 5 min since the spill. At a wind speed of 7.5 km/h there remain 330 min before the puff reaches the maximum downwind hazard distance of 42 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, hydrogen chloride and hydrochloric acid will dissolve rapidly. Mixing takes place and the spill is diluted. In the case of hydrogen chloride, mixing will be accompanied by violent boiling and vapour release. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate the pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water. As hydrogen chloride/hydrochloric acid is denser than water, the maximum concentration would be expected near the bottom during the initial period after the spill.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d <100) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 Nomograms. The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

Figure 26:	distance versus time for a range of average stream velocities
Figure 27:	hydraulic radius versus channel width for a range of stream depths
Figure 28:	diffusion coefficient versus hydraulic radius for a range of average stream velocities

FIGURE 23

HYDROGEN CHLORIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

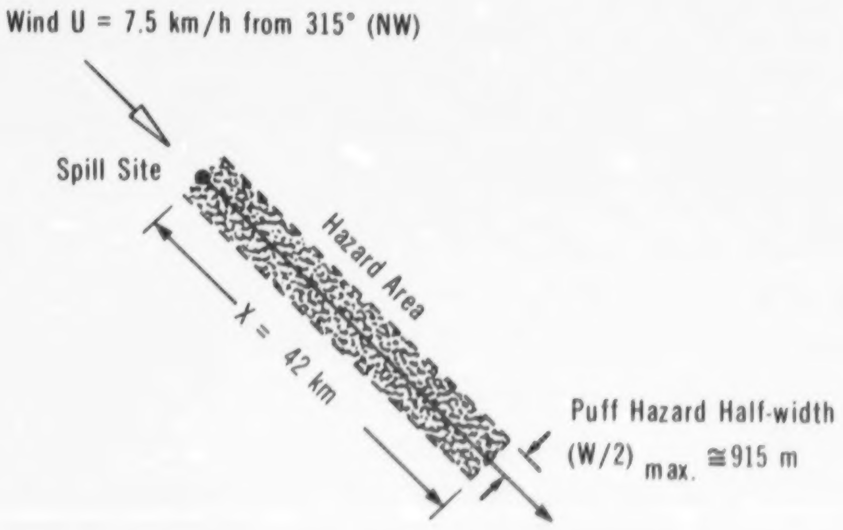
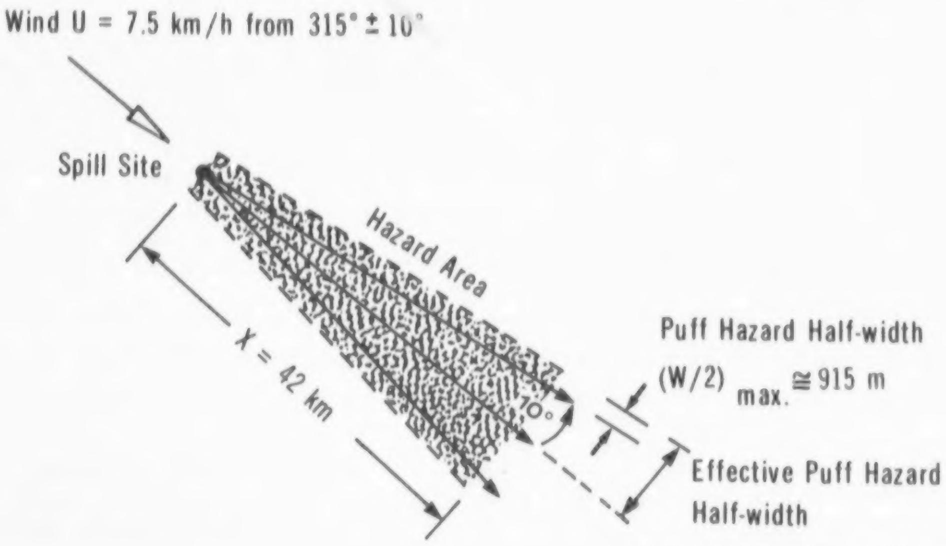

Wind U = 7.5 km/h from 315° (NW)
Spill Site
Hazard Area
X = 42 km
Puff Hazard Half-width
(W/2) max. ≅ 915 m

FIGURE 24

HYDROGEN CHLORIDE

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X = 42 km
10°
Puff Hazard Half-width
(W/2) max. ≅ 915 m
Effective Puff Hazard
Half-width

$= X \times 1000 \times \tan 10° + (W/2)_{max.}$

$= 42\ \text{km} \times 1000 \times \tan 10° + 915\ \text{m}$

$= 8{,}300\ \text{m}$

Figure 29:	alpha* versus diffusion coefficient for various time intervals
Figure 30:	alpha versus delta* for a range of spill sizes
Figure 31:	maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 32:	volume versus radius for the hazard zone for a range of lake depths
Figure 33:	average concentration versus volume for the hazard zone for a range of spill sizes

The flow chart in Figure 25 outlines the steps required to estimate downstream concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 26 through 31) are described in the following subsections.

5.4.2.1 Nomograms for non-tidal rivers.

Figure 26: Distance versus time. Figure 26 presents a simple relationship between average stream velocity, time, and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest, at some distance (X) downstream of the spill, can be readily obtained from Figure 26.

Figure 27: Hydraulic radius versus channel width. The model used to estimate downstream pollutant concentrations is based on an idealized rectangular channel of width (W) and depth (d). The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 27 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

Figure 28: Diffusion coefficient versus hydraulic radius. Figure 28 permits calculation of the longitudinal diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 27 and the average stream velocity (U).

Figure 29: Alpha versus diffusion coefficient. Figure 29 is used to estimate a conversion factor, alpha (α), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

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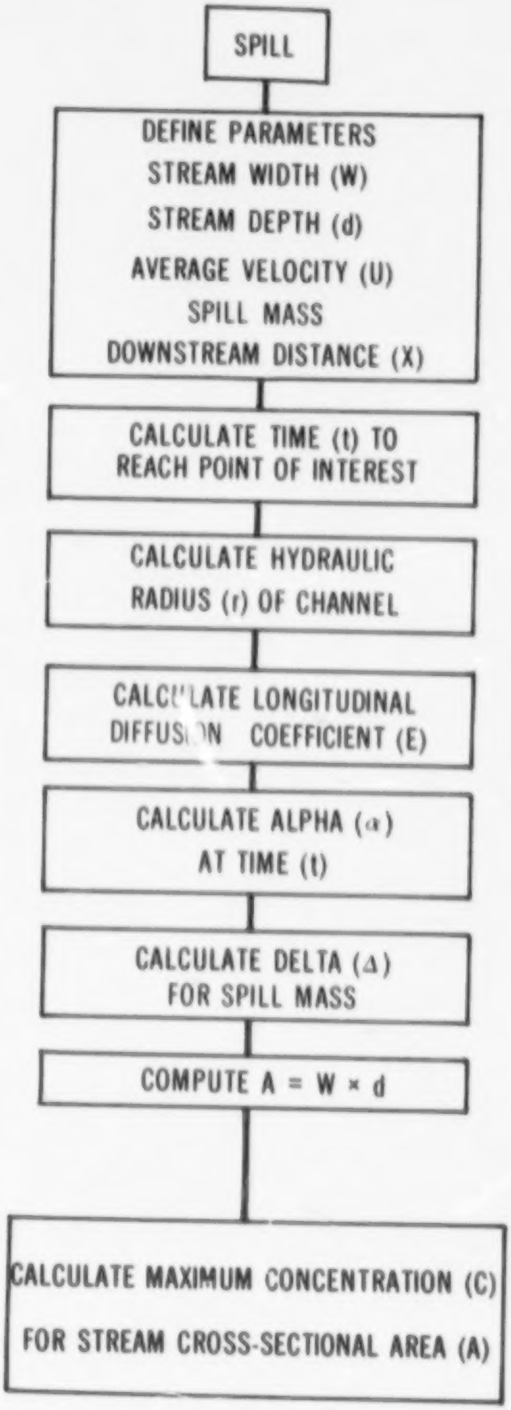
* Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentrations.

FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C)
FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = __________ m

d = __________ m

U = __________ m/s

MASS = __________ tonnes

X = __________ m

Step 2: Use Figure 26

t = __________ minutes

Step 3: Use Figure 27

r = __________ m

Step 4: Use Figure 28

E = __________ m^2/s

Step 5: Use Figure 29

α = __________

Step 6: Use Figure 30

Δ = __________

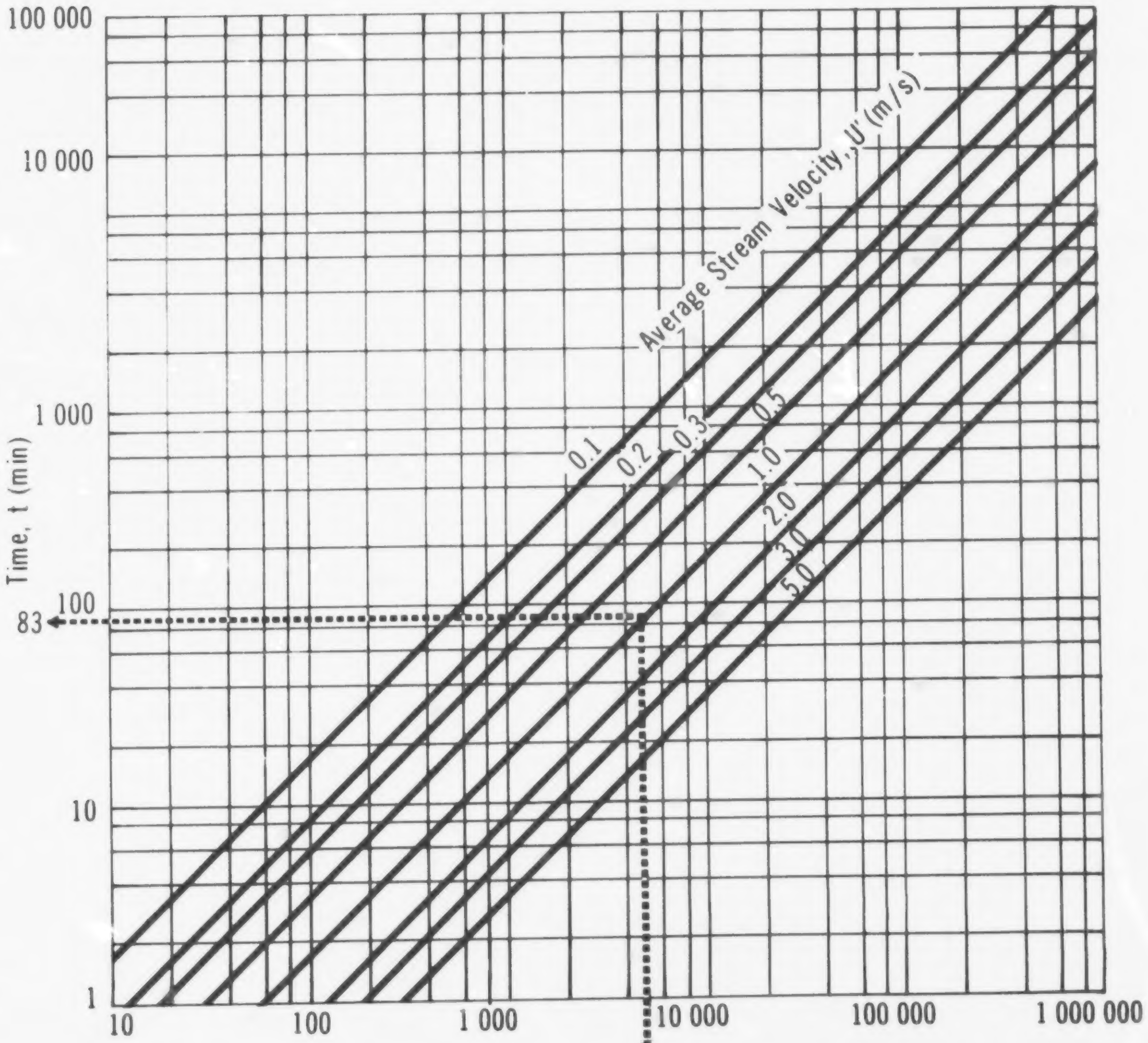
Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ m^2

Step 8: Use Figure 31

C = __________ ppm

TIME vs DISTANCE



HYDRAULIC RADIUS VS CHANNEL WIDTH

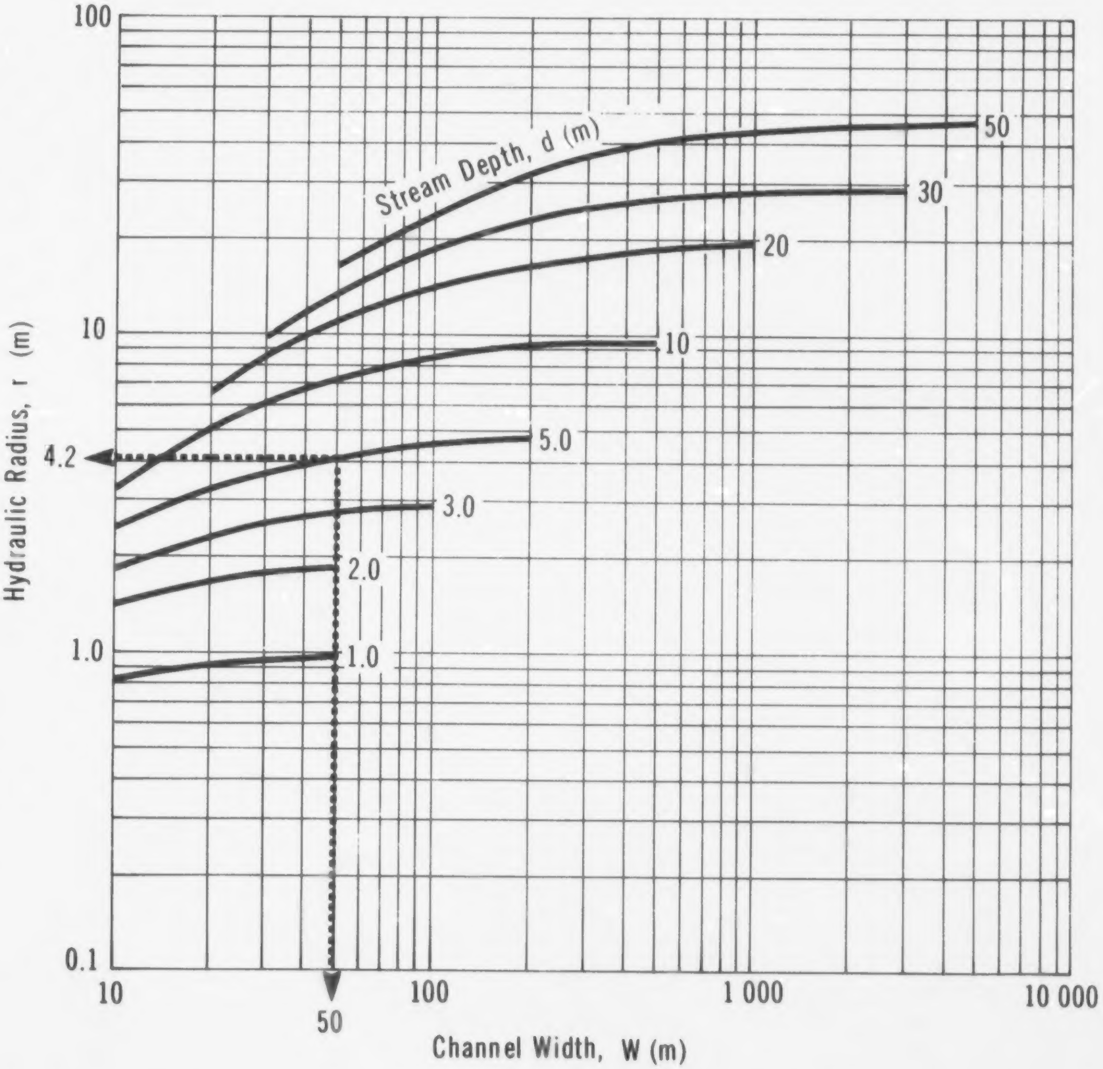
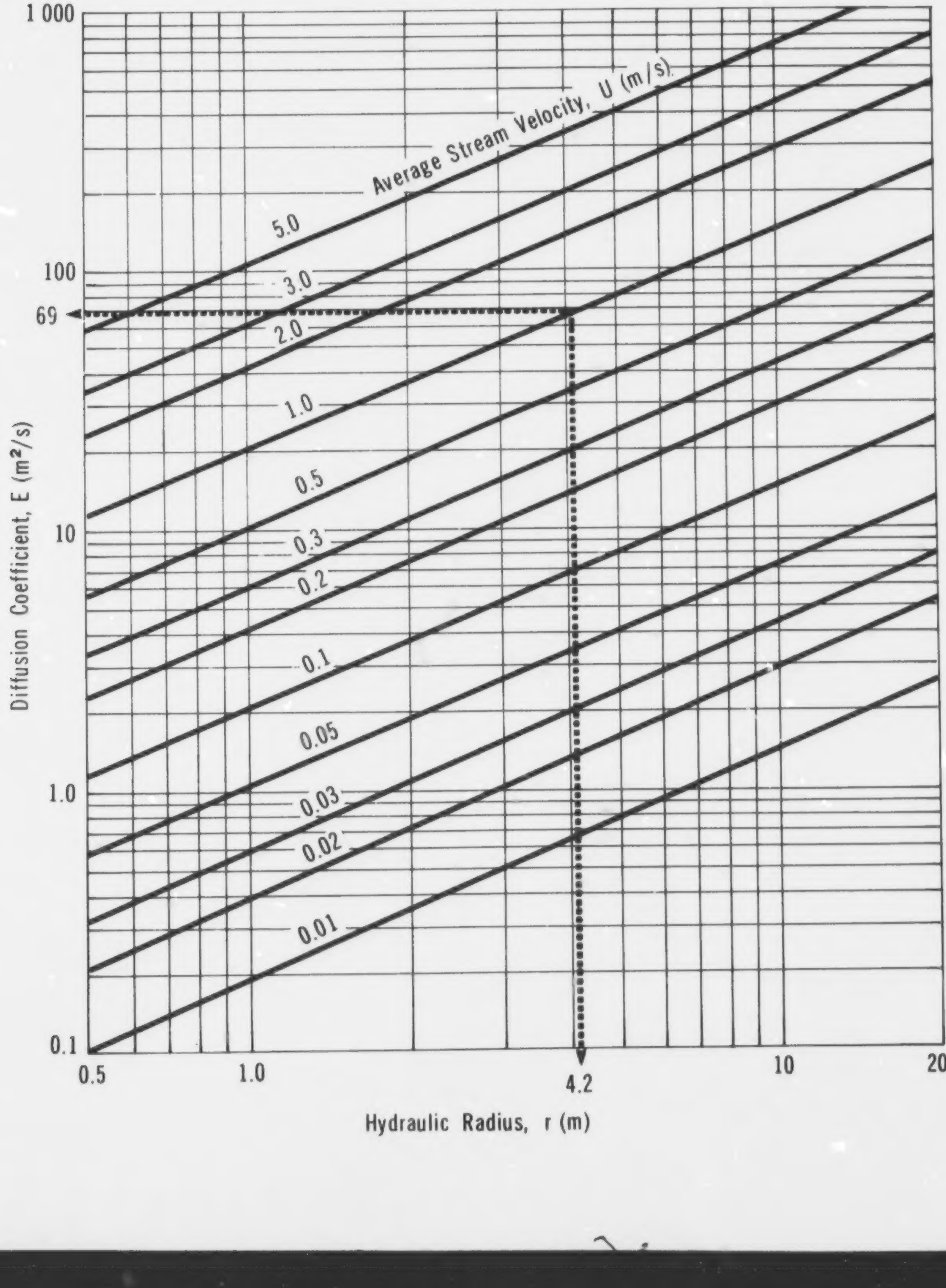


FIGURE 28

DIFFUSION COEFFICIENT VS HYDRAULIC RADIUS



ALPHA vs DIFFUSION COEFFICIENT

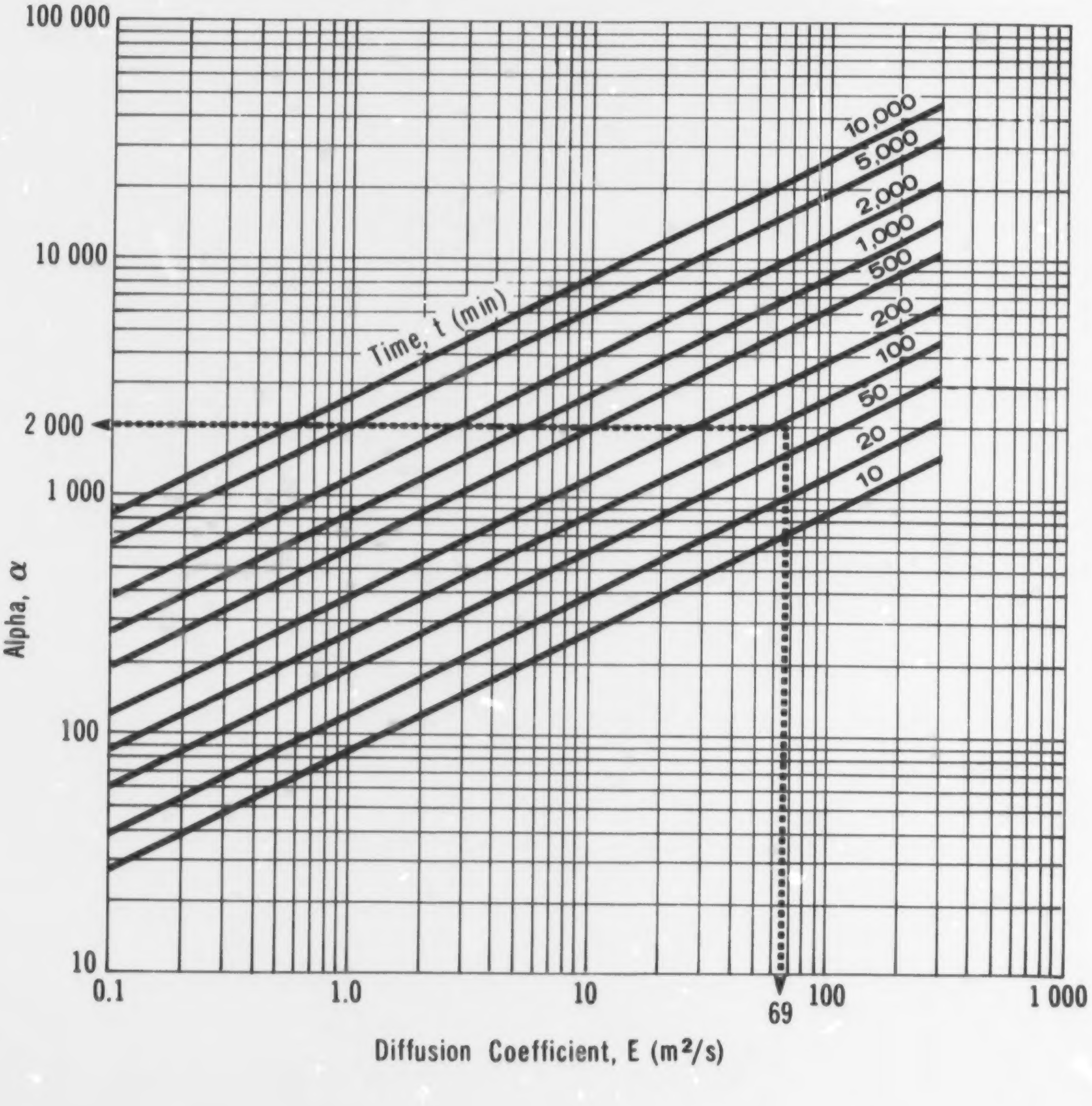


Figure 30: Alpha versus delta. A second conversion factor, delta (Δ), must be estimated from Figure 30 to allow determination of the pollutant concentration at the point of interest. Delta (Δ) is a function of alpha (α) and the spill size.

Figure 31: Maximum concentration versus delta. Figure 31 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta (Δ) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 31 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

5.4.2.2 Nomograms for lakes or still water bodies.

Figure 32: Volume versus radius. The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water in the cylinder can be obtained from Figure 32. The radius (r) represents the distance from the spill to the point of interest.

Figure 33: Average concentration versus volume. For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 33 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

5.4.3 Sample Calculations.

5.4.3.1 Pollutant concentration in non-tidal rivers. A 20 tonne spill of 38 percent hydrochloric acid solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s

ALPHA vs DELTA

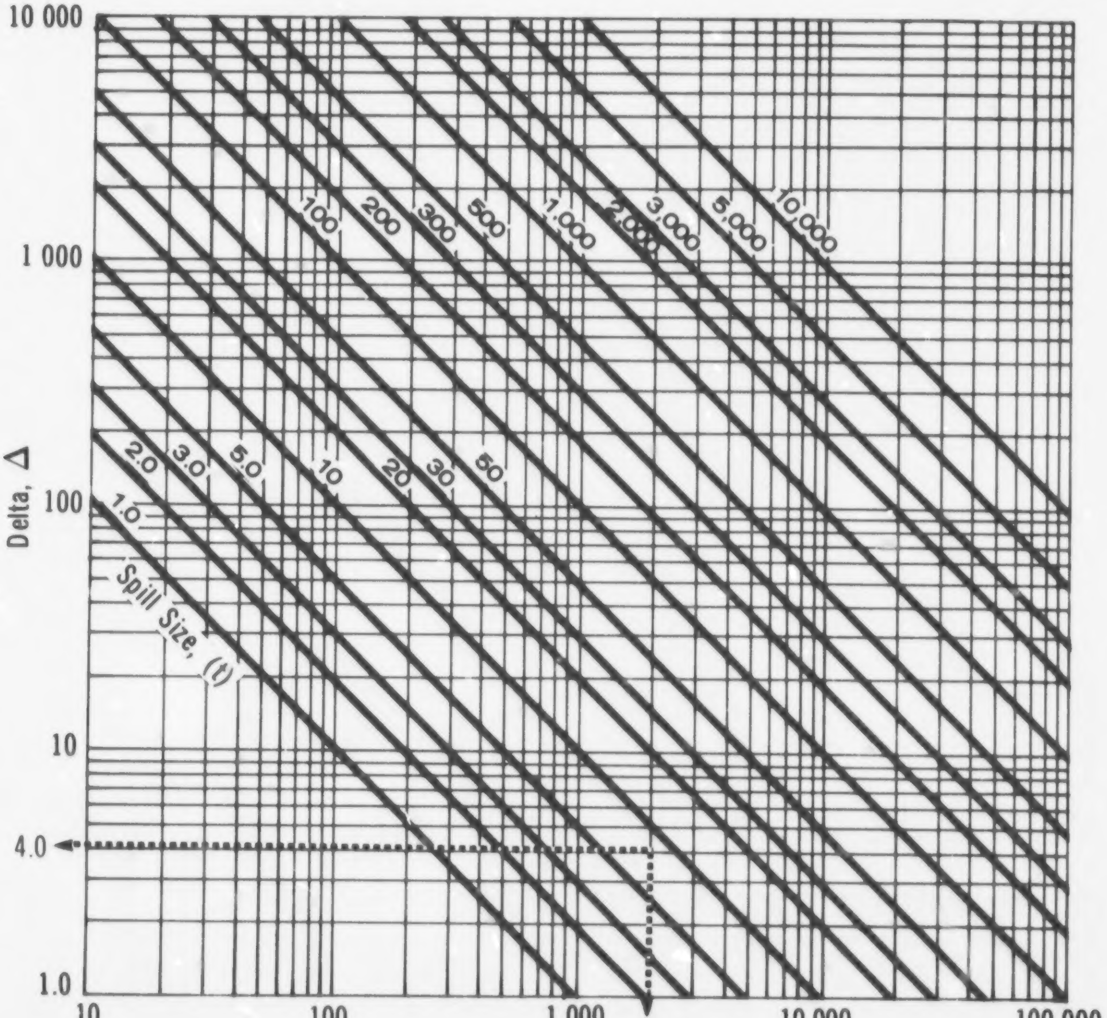
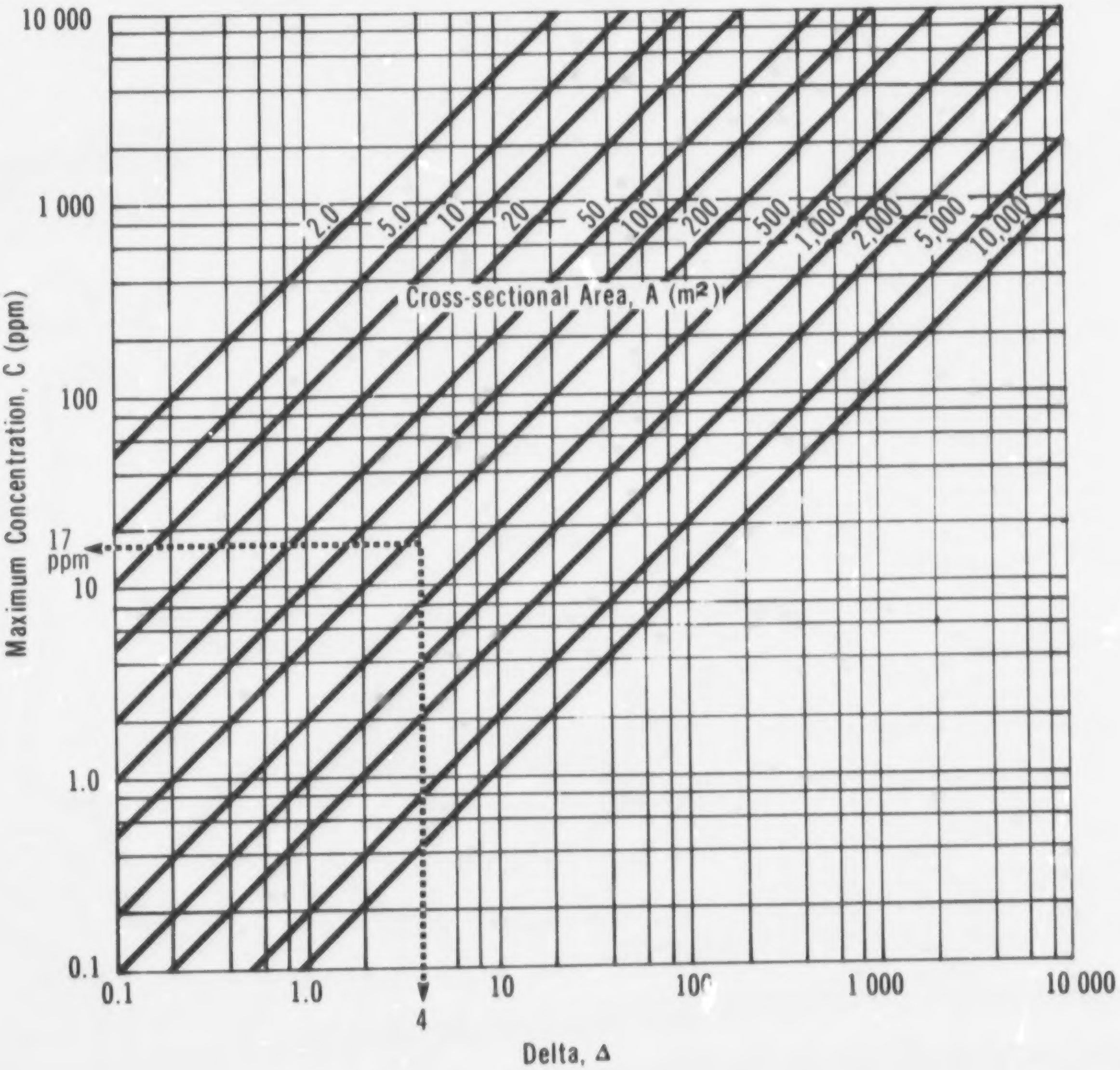
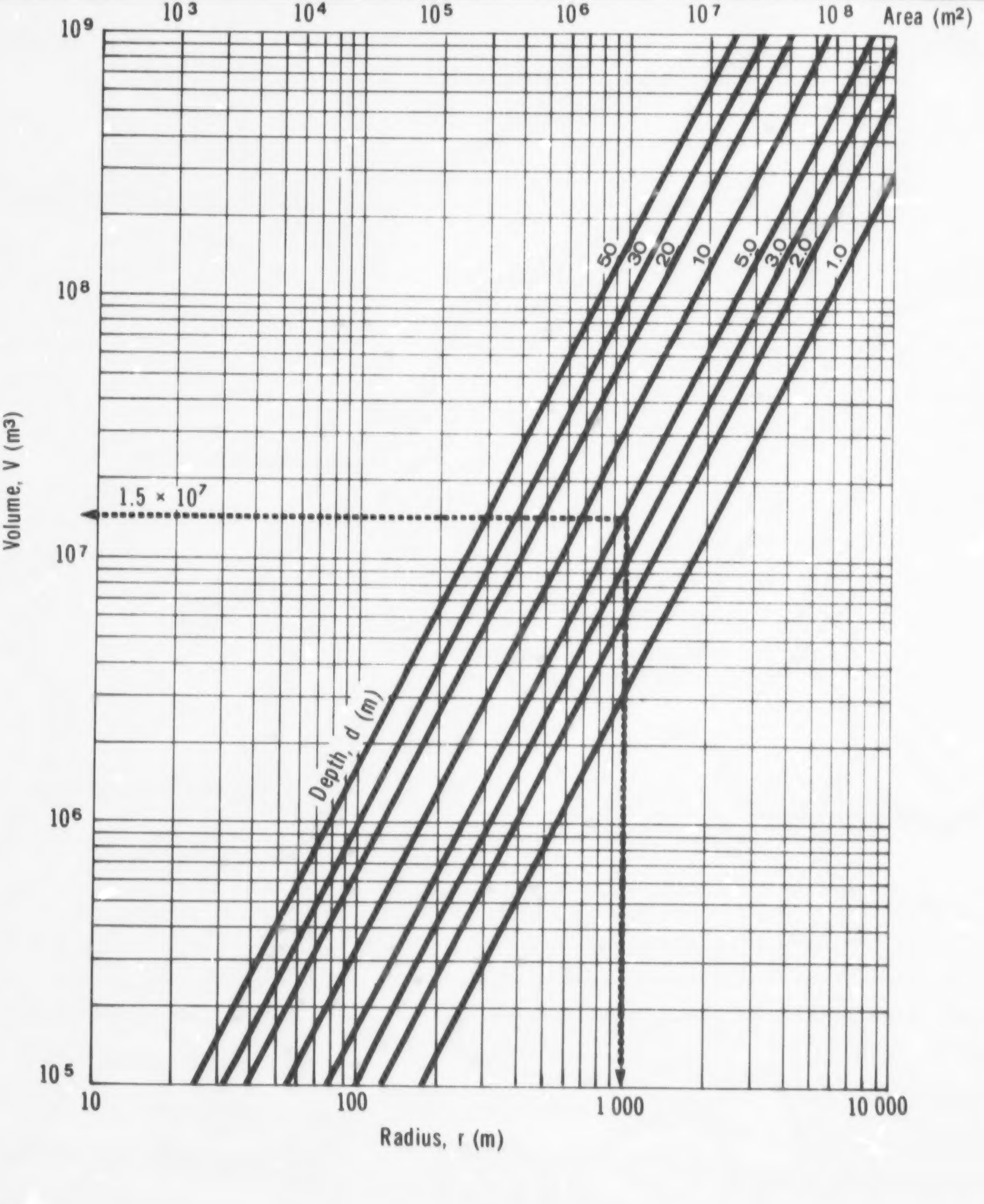


FIGURE 31

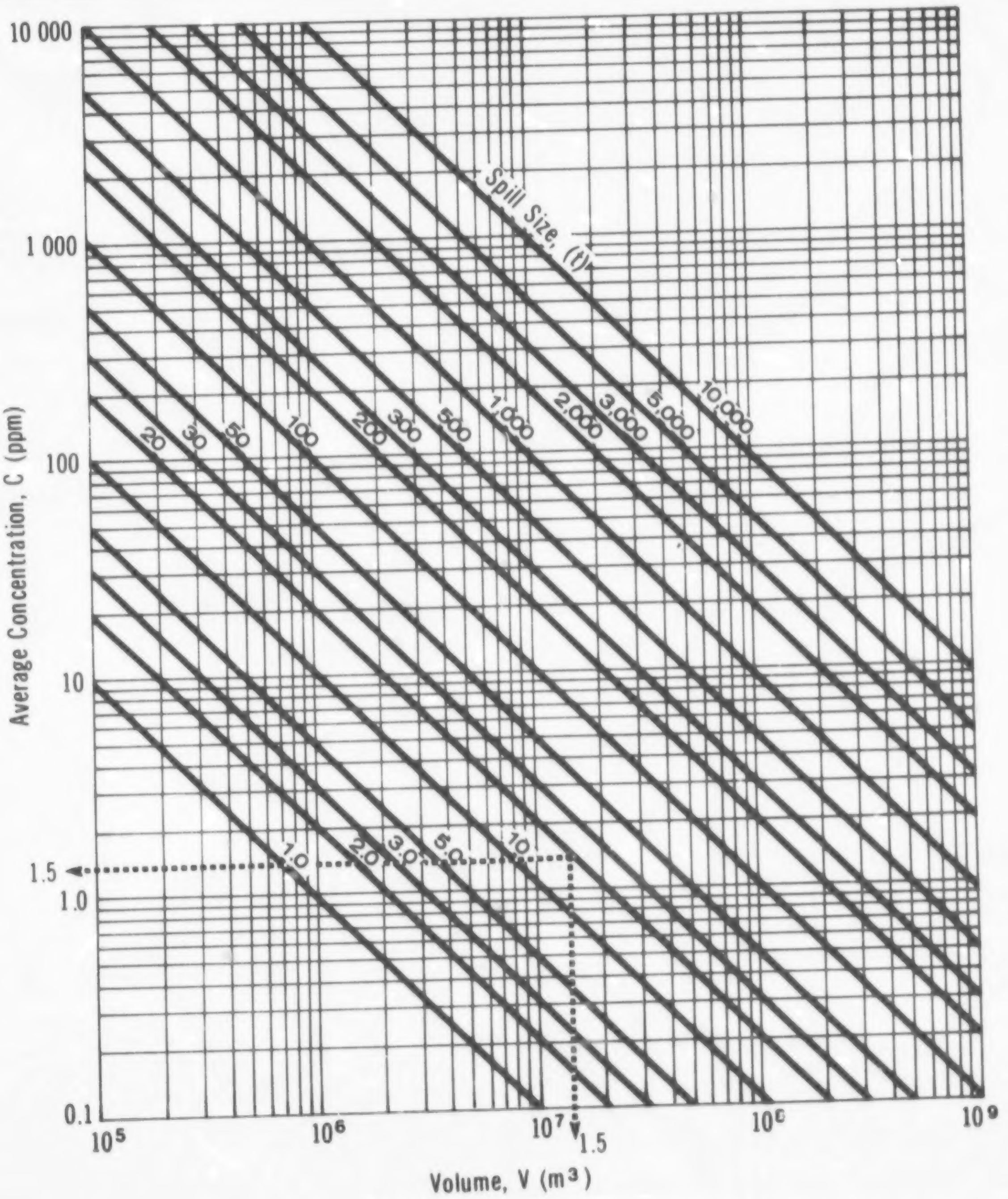
MAXIMUM CONCENTRATION vs DELTA



VOLUME vs RADIUS



AVERAGE CONCENTRATION vs VOLUME



- Spill mass = 20 tonnes of 38 percent solution, equivalent to 7.6 tonnes of pure hydrogen chloride
- X = 5000 m

Step 2: Calculate the time to reach the point of interest

- Use Figure 26
- With X = 5000 m and U = 1 m/s, t = 83 min

Step 3: Calculate the hydraulic radius (r)

- Use Figure 27
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate the longitudinal diffusion coefficient (E)

- Use Figure 28
- With r = 4.2 m and U = 1 m/s, E = 69 m^2/s

Step 5: Calculate alpha (α)

- Use Figure 29
- With E = 69 m^2/s and t = 83 min, α = 2000

Step 6: Calculate delta (Δ)

- Use Figure 30
- With alpha (α) = 2000 and spill mass = 7.6 tonnes (pure hydrogen chloride), delta (Δ) = 4

Step 7: Compute the stream cross-sectional area (A)

- A = W x d = 50 x 5 = 250 m^2

Step 8: Calculate the maximum concentration (C) at the point of interest

- Use Figure 31
- With Δ = 4 and A = 250 m^2, C = 17 ppm

5.4.3.2 **Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of anhydrous hydrogen chloride, has occurred in a lake. The point of interest is located on the shore approximately 1000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m

- r = 1000 m
- spill mass = 20 tonnes
- X = 5000 m

Step 2: Determine the volume of water available for dilution

- Use Figure 32
- With r = 1000 m, d = 5 m, the volume is approximately 1.5×10^7 m^3

Step 3: Determine the average concentration

- Use Figure 33
- With V = 1.5×10^7 m^3 and spill mass = 20 tonnes, the average concentration is 1.5 ppm

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of hydrogen chloride/hydrochloric acid onto soil and the transport downward through the soil are presented here.

Anhydrous hydrogen chloride has a boiling point of -85.05°C; consequently, extensive evaporation will occur when it is spilled onto soil. Therefore, with regard to infiltration into the soil, only hydrochloric acid is considered.

When the aqueous solution is spilled onto soil, it will begin to infiltrate. However, since hydrochloric acid is miscible with water, the presence of water in the soil or falling as precipitation at the time of the spill will influence the rate of movement in the soil, and dilution through mixture with water will decrease the viscosity more than the mass density. This will have the net effect of increasing the velocity of downward movement in the soil. However, if the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off and/or evaporate away.

For this work, the soils have been assumed to be at field capacity. This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents "worst case" analysis.

During transport through the soil, hydrochloric acid will dissolve some of the soil material, in particular that of a carbonate base. During this process, the acid will be neutralized to some degree; however, significant amounts of acid are expected to remain for transport down toward the groundwater table. The analysis used here neglects these retarding factors. This is particularly appropriate for the chloride ion.

Upon reaching the groundwater table, the acid will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the acid concentration somewhat. This is shown schematically in Figure 34.

5.5.2 Equations Describing Hydrochloric Acid Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Hydrochloric Acid in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

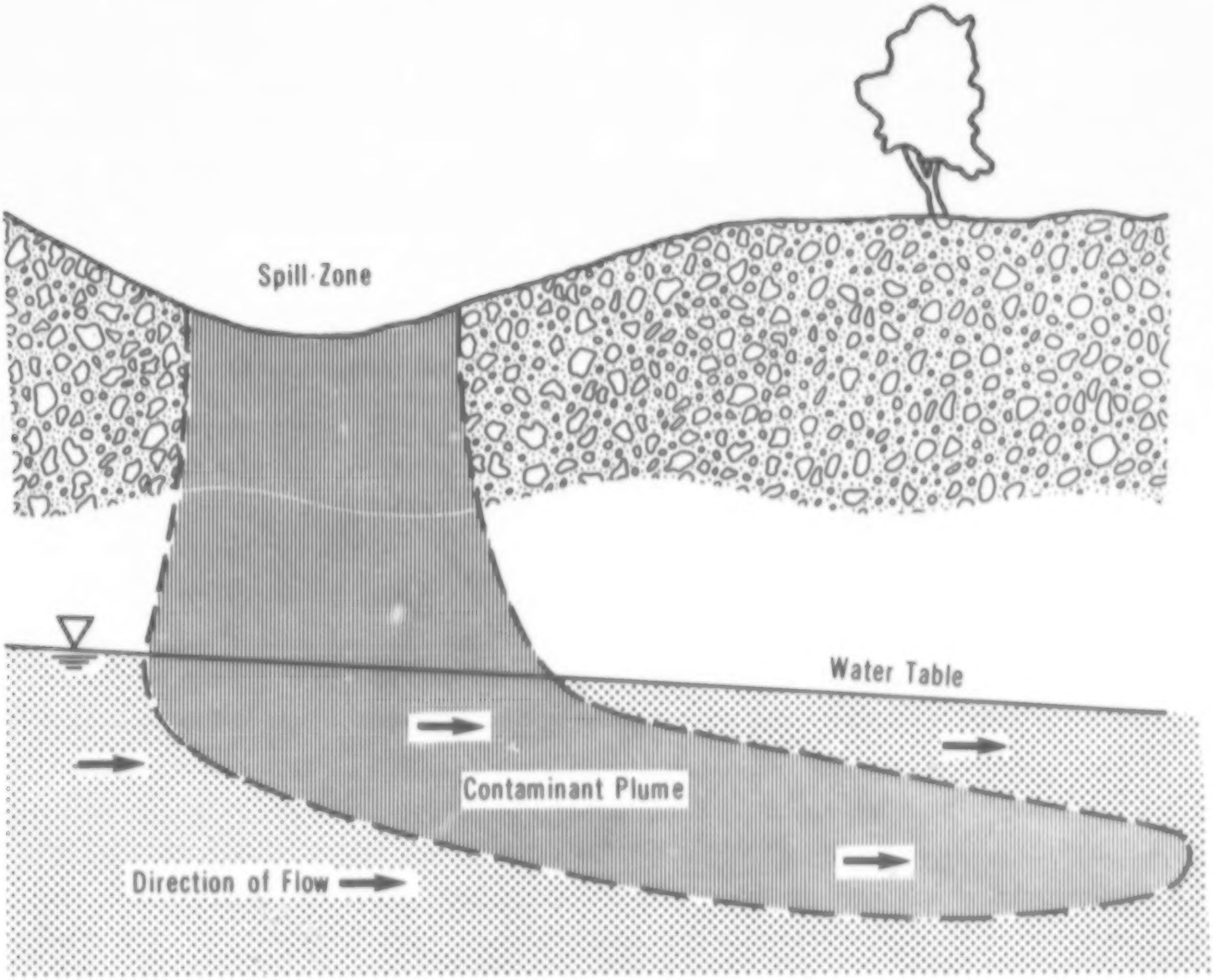
where: k = intrinsic permeability of the soil (m^2)
ρ = mass density of the fluid (kg/m^3)
μ = absolute viscosity of the fluid (Pa·s)
g = acceleration due to gravity = 9.81 m/s^2

The fluids modelled here are 31.5 percent by weight hydrochloric acid and water. The water calculations represent the extreme as hydrochloric acid is diluted.

	Hydrochloric Acid (31 percent)		Water
Property	20°C	4°C	20°C
Mass density (ρ), kg/m^3	1150	1160	998
Absolute viscosity (μ), Pa·s	2.0×10^{-3}	2.4×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(0.56 \times 10^7)k$	$(0.47 \times 10^7)k$	$(0.98 \times 10^7)k$

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

SCHEMATIC SOIL TRANSPORT


Spill·Zone
Water Table
Contaminant Plume
Direction of Flow

Soil: Coarse Sand
–Porosity (n) = 0.35
–Intrinsic Permeability (k) = 10^{-9} m^2
–Field Capacity (θ_{fc}) = 0.075

Property	Soil Type Coarse Sand	 Silty Sand	 Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 **Penetration Nomograms.** Nomograms for the penetration of hydrochloric acid into the unsaturated zone above the groundwater were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flowchart for the use of the nomograms is presented in Figure 35. The nomograms are presented as Figures 36, 37, and 38. The water line on the nomograms represents the maximum penetration of water at 20°C in time t_p. It is a limiting condition as hydrochloric acid becomes diluted with water.

5.5.6 **Sample Calculation.** A 20 tonne spill of 31.5 percent hydrochloric acid has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 25 minutes after the spill and check the corresponding evaporation loss.

Solution

Step 1: Define parameters

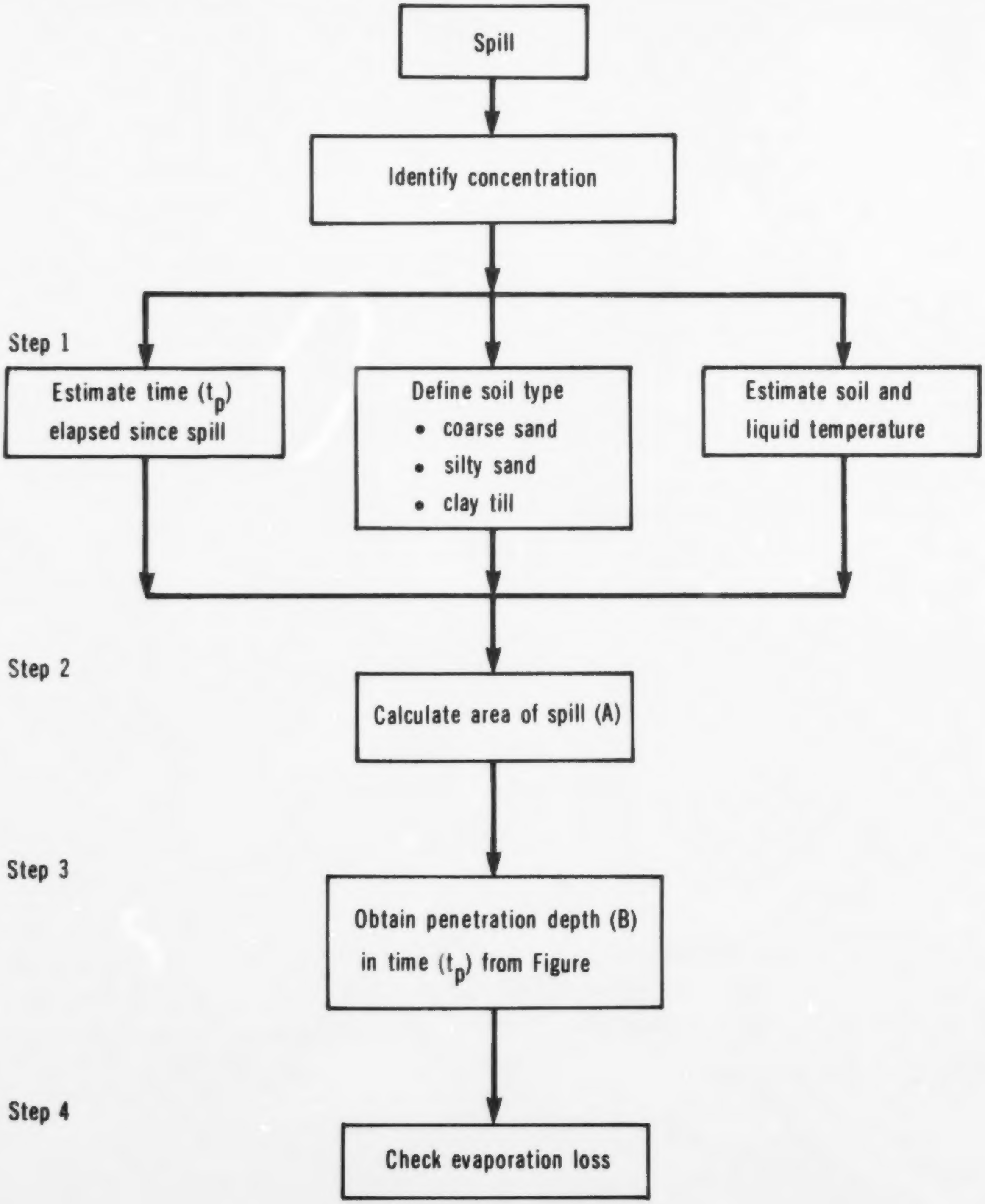
- Mass spilled = 20 000 kg (20 tonnes)
- $T = 20°C$
- $r = 8.6$ m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 25 min

Step 2: Calculate area of spill

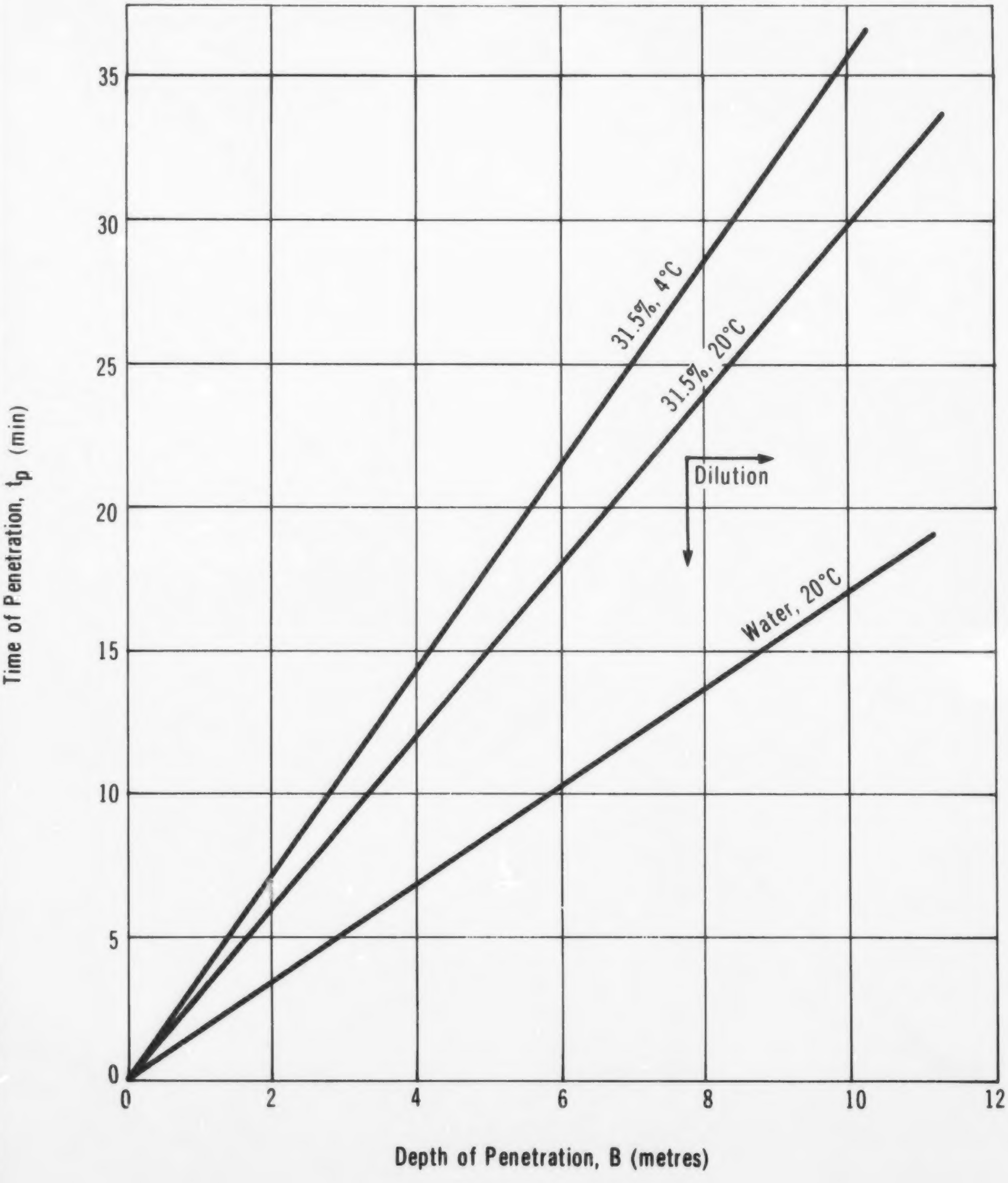
- $A = \pi r^2 = 232\ m^2$

FIGURE 35

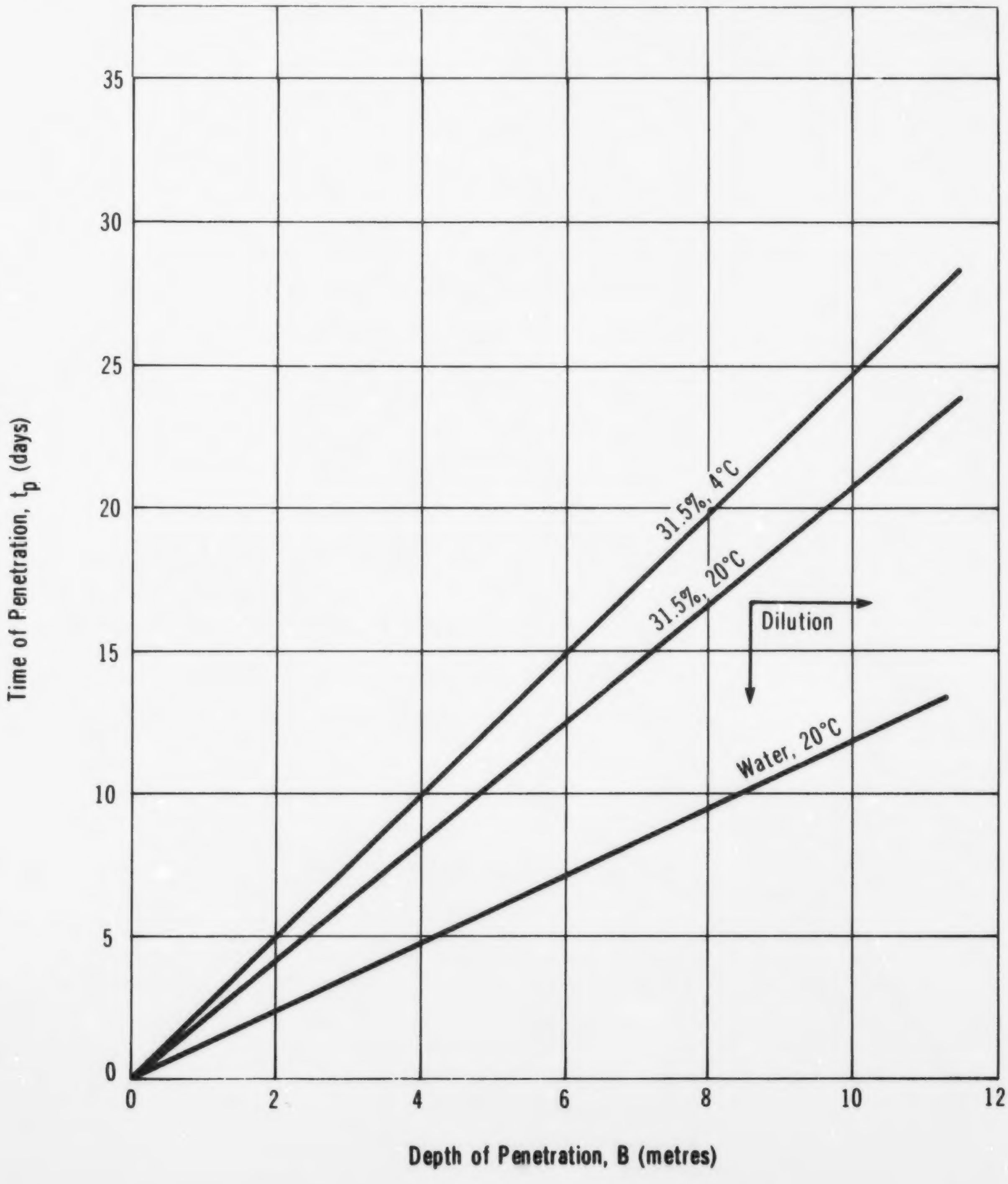
FLOWCHART FOR NOMOGRAM USE


Spill
Identify concentration
Step 1
Estimate time (t_p) elapsed since spill
Define soil type
• coarse sand
• silty sand
• clay till
Estimate soil and liquid temperature
Step 2
Calculate area of spill (A)
Step 3
Obtain penetration depth (B) in time (t_p) from Figure
Step 4
Check evaporation loss

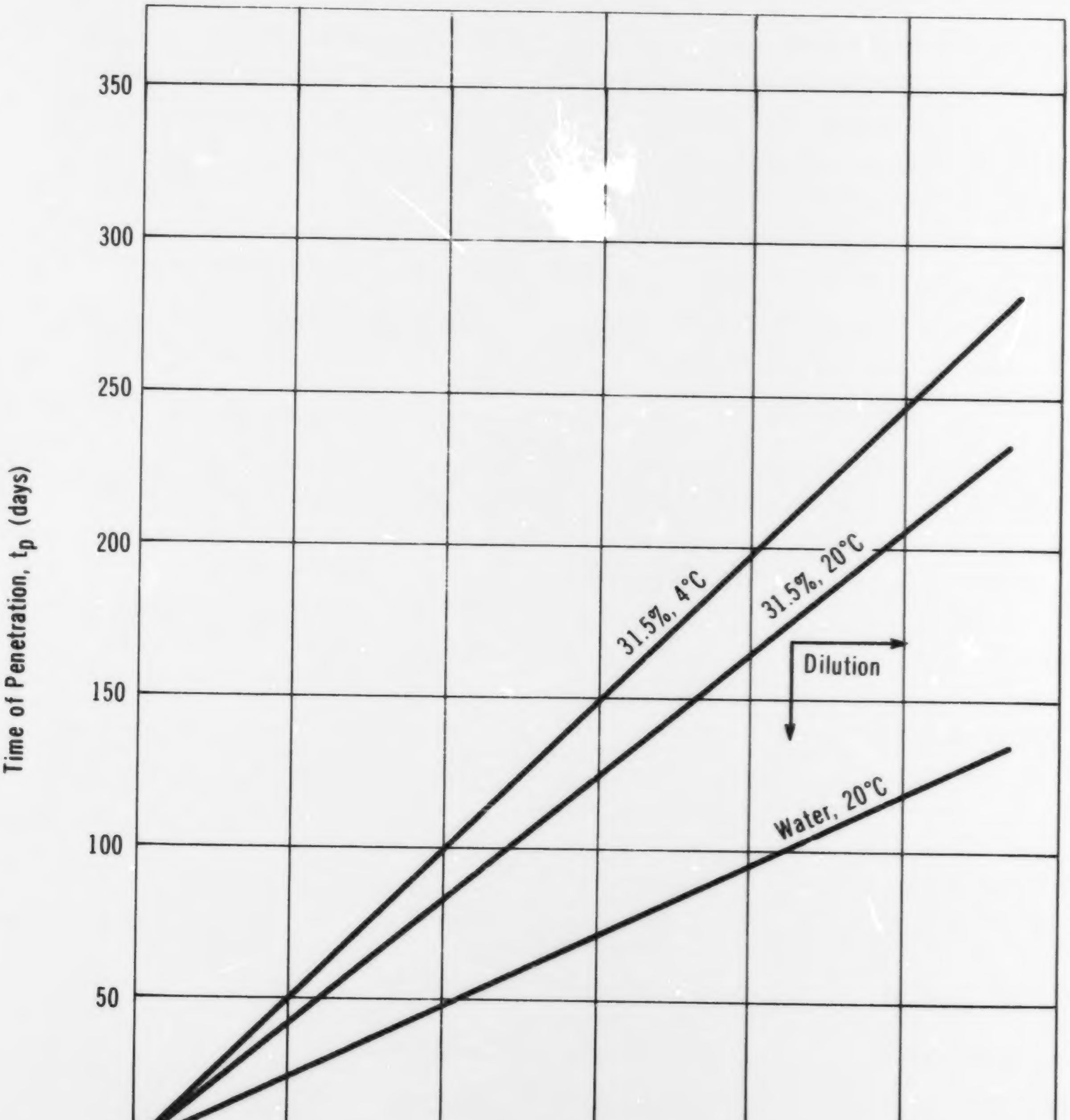
PENETRATION IN COARSE SAND



PENETRATION IN SILTY SAND



PENETRATION IN CLAY TILL



Step 3: Estimate depth of penetration (B) at time (t_p)

- For coarse sand, B = 8.3 m at t_p = 25 min
- Groundwater table has not been reached in this time

Step 4: Check evaporation loss

- Evaporation of 31.5 percent hydrochloric acid is negligible after 25 min under the spill conditions

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 **Water.** Hydrogen chloride is perceived by the sense of taste at 32 mg/L (MHSSW 1976), although this threshold is dependent upon the buffering action of the water. Water acquires a sour taste at pH 3.9 or below, except in highly buffered solutions (PB 216658). Levels in excess of 4000 mg/L can cause injury to livestock (PB 216658); Todd (1970) and OHM-TADS (1981) give a maximum level of hydrochloric acid in water for livestock as 3000 mg/L. The threshold level for use as irrigation water is 100 mg/L (Todd 1970; PB 216658).

6.1.2 **Air.** Canada limits airborne hydrogen chloride to 100 $\mu g/m^3$ (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 **U.S. Toxicity Rating.** No TL_m 96 (4-day median lethal toxicity rating) has been assigned. The lowering of pH causes death to aquatic life (OHM-TADS 1981). The lower tolerable limit for most fish is pH 5, and for the most resistant species, pH 4. At a pH below 5, specialized flora and fauna may develop (PB 216658).

6.2.2 Measured Toxicities.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
10	24	Trout	100% mortality		MHSSW 1976
pH 4.6	96	Stickleback	TL_m, death at 10.5 h	2°C	WQCDB-5 1973
pH 5 (as HCl)	9 days	Stickleback	100% mortality	-	OHM-TADS 1981
pH 4 (as HCl)	10.5	Stickleback	100% mortality	-	OHM-TADS 1981
pH 3 (as HCl)	80 min	Stickleback	100% mortality	-	OHM-TADS 1981
pH 3.6 (as HCl)	96	Sunfish	TL_m	20°C	OHM-TADS 1981

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
pH 4 (as HCl)	96	Goldfish	TL_m	20°C	OHM-TADS 1981
3.6	48	Sunfish	lethal	distilled	WQC 1963
166	4	Goldfish	killed	hard	WQC 1963
60 to 80	24	Creek chub	critical range: low value - lived for 24 h; high death rate at upper value	Detroit River water	WQC 1963
3.65	24	Carp, shiners suckers	lethal		WQC 1963
8	24	Sunfish	lethal		WQC 1963
178	1 to 2	Goldfish	lethal		Wilber 1969
Fish Toxicity Tests					
282	96	Mosquito fish	TL_m	farm pond; high turbidity	WQCDB-3 1971
0.018	6	Stickleback	TL_m		Klein 1957
4	6	Minnow	LD_{50}	distilled	WQC 1963
100	6	Minnow	LD_{50}	hard	WQC 1963
Insects					
not stated	96	Stone flies	death	pH 2.9 to 4.04	WQCDB-5 1973
not stated	96	Dragonflies	death	pH 3.18 to 3.35	WQCDB-5 1973
not stated	96	Mayflies	death	pH 4.35 to 5.05	WQCDB-5 1973
not stated	96	Caddis flies	death	pH 3 to 3.35	WQCDB-5 1973
Microorganisms					
65	1 to 4	*Daphnia magna*	survival time	soft	Wilber 1969
62	not stated	*Daphnia magna*	immobilization	Lake Erie water, 25°C	Klein 1957
56	17-72	*Daphnia magna*	20% survival	soft, static	Wilber 1969

6.2.2.2 Saltwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Invertebrates					
260	48	Brown shrimp	LC_{50}	aerated	WQCDB-5 1973
240	48	Shore crab	LC_{50}	aerated	WQCDB-5 1973
100 to 330	48	Pogge	LC_{50}	aerated	Portman 1970
100 to 330	48	Starfish	LC_{50}	aerated	Portman 1970
330 to 1000	48	Cockle	LC_{50}	aerated	Portman 1970
100 to 330	48	Shrimp	LC_{50}	aerated	Portman 1970

6.3 Toxicity to Other Biota

6.3.1 **Livestock.** Hydrochloric acid has a powerful corrosive action on the living tissues of livestock; however, fatalities from this and other strong acids are rare amongst livestock (Clarke 1975). The maximum level reported to be the toxicity threshold for extended use for livestock is 1500 mg/L (Todd 1970), which is well below the level above which injury would be expected (4000 mg/L).

6.3.2 **Plants.** Plant life may be exposed to hydrogen chloride from an accidental spill in the form of vapour, aerosol, liquid or aqueous solution. Exposure to liquefied hydrogen chloride would be localized and would certainly be lethal to most, if not all, plant life contacted. Due to the hygroscopic nature of the anhydrous gas, vapour being released from a damaged container or from a pool will gradually be converted to the aerosol as it combines with the moisture of the atmosphere. The extent of damage to plant life will vary according to dose and atmospheric conditions; the area of coverage can be widespread as the vapour/aerosol cloud is dispersed and carried away from the release site by the wind. The catastrophic release of aqueous hydrogen chloride (hydrochloric acid) will be localized with respect to the movement of the liquid on land; however, aerosol coverage may be more widespread. Damage will be that typical of aqueous acid and aerosol. Comments regarding the nature of the damage to plant life by hydrogen chloride were gleaned from three sources, with by far the most comprehensive data being concerned with fumigation studies involving hydrogen chloride gas of various concentrations at various atmospheric humidities and temperatures.

In general, there is a lack of detailed information on the effects of hydrogen chloride gas on plants. It is obvious, however, that the gas can have serious effects on plant life at low concentrations. Many of the conclusions derived from the early work are no longer tenable, particularly those dealing with dose response, because of improper fumigation methods. The field observations are presumably still valid. It is clear that plants respond differently to a gas and to an acid aerosol, so the determination of the form of the chloride reaching the plant is as important as the degree of exposure. Recent work indicates that chronic effects can be expected at 0.40 ppm and acute effects at a few parts per million (~1-20 ppm), depending on the species. Relative humidity appears to be the governing factor in plant response. There appears to be a threshold of relative humidity above which plants will incur twice as much damage at a given dose. It appears that, at least in the gas phase, hydrogen chloride enters through the stomata and accumulates as chlorides in the foliar parts of the plant. It is not known, however, whether the injury is due to the acidity of the gas, the toxicity of the chloride, or both.

Conc. (ppm)	Time (hours)	Species	Result	Date of Work	Reference
EXPERIMENTS WITH HCl GAS - ACUTE					
Released from HCl(aq.), no air circulation	-	Broadleaf species (roses, buffalo currant, beech, birch, maple, oak viburnum, apple, pear, cherry)	Discoloration on margin of leaves and spotting in central portion of leaves	1903 + prior	NAS 1976
"		Narrowleaf species (grain crops, meadow-grass)	Tips and edges of leaves turn brown; higher concentration caused leaves to turn brown and go limp	"	"
"		Conifer (larch, spruce, fir, pine)	Discoloured needle tips (yellowing and browning), flower parts affected (blue colouring in chicory and cornflowers)	"	"

onc. (ppm)	Time (hours)	Species	Result	Date of Work	Reference
-	-	Begonia	Margin of leaf tissue turned brown-orange, premature leaf abscission, necrotic spots on surface of leaves	1968/69	NAS 1976
-	-	Northern hardwood species	Chlorotic flecking of upper leaf surfaces, red-brown to black necrotic spots on ieaves	"	"
"		Conifer species	Tan necrotic flecks and distortion of leaves, broad leaves exhibited cupping	"	"
Experimental Conditions: (27°C, 78-85% relative humidity, light intensity 1.4 x 10^4 ergs/(cm^2·s)					
Conifers					
8	4	White pine	Tip necrosis on needles	1969	NAS 1976
12	4	Balsam, Douglas fir	Tip necrosis on needles	"	"
19	4	Norway spruce	Tip necrosis on needles	"	"
18	4	Austrian pine	No injury		
43	4	Arborvitae	No injury		
Broadleaf species					
3	4	Tuliptree	Marginal and interveinal necrosis and necrotic flecking	"	"
6	4	European black alder, black cherry	"	"	"
7	4	Sugar maple, Norway maple	"	"	"
to 13	4	Red oak	Not injured	"	"
4	2	Tomato (Bonny Best)	70% rel. hum., 30°C - severe bronzing	"	"

Conc. (ppm)	Time (hours)	Species	Result	Date of Work	Reference
10	2	Tomato (Bonny Best)	50% rel. hum., 31°C - severe bronzing	1969	NAS 1976
5	2	"	81% rel. hum., 33°C - marginal leaf necrosis, injury to the petiole	"	"
10	2	"	55% rel. hum., 31°C - marginal leaf necrosis, injury to the petiole	"	"
3	2	"	65-72% rel. hum., 31-33°C - glazing on underside of leaf, leaf tipburn, necrotic flecking	"	"
8	3		35% rel. hum., 31-33°C - glazing on underside of leaf, leaf tipburn, necrotic flecking	"	"
2-5	2-3	"	55-60% rel. hum., 30-31°C - no visible injury	"	"
8.5	3	"	23% rel. hum., 30-31°C - no injury	"	"
8-23	4	Chrysanthemum (Neptune)	65-70% rel. hum., 30-31°C - bronzing (severe injury)	"	"
8-23	2	"	"		
3.5	3	"	65% rel. hum., 31°C - marginal necrosis	"	"
8.5	3	"	45% rel. hum., 31°C - petiole injury	"	"
6	5	"	60% rel. hum., glazing on underside of leaf, tipburn, necrotic flecking	"	"
12	2	"	52% rel. hum., glazing on underside of leaf, tipburn, necrotic flecking	"	"
2.7	2 or 3	"	60% rel. hum., 30°C, no injury	"	"

Conc. (ppm)	Time (hours)	Species	Result	Date of Work	Reference
8-10	2	Tomato (Bonny Best)	40-50% rel. hum. - No symptoms noticed, 20-30% stimulation of respiration detected	1970	NAS 1976
8-10	-		≤40% rel. hum. - Photosynthesis rates 90% of control plants, no injury	"	"
~2.6	2	Bean (Pinto III)	Threshold concentration for injury	1972	NAS 1976
EXPERIMENTS WITH HCl GAS - CHRONIC					
0.70	10 h/d, 2 d	Tomato (Bonny Best)	Chlorosis - interveinal, younger leaves and leaves of intermediate maturity, chlorophyll and pheophytin were reduced and transpiration rates were slightly decreased, respiration rate was unchanged	1970	NAS 1976
0.40	8 h/d, 6 d	"	No visible damage to greenhouse-grown plants during the winter; on greenhouse-grown plants during May and June, chlorosis developed after the 3rd and 4th consecutive fumigation	"	"
EXPERIMENTS WITH HYDROCHLORIC ACID					
-	-	Waterweed, beans, crabs red beeches	Dipped plants in aqueous HCl and CO_2 and counted bubbles - concluded hydrochloric acid decreases assimilation	1903	NAS 1976

6.3.2.1 Crops.

Conc. (mg/m^3)	Time (hours)	Species	Result	Reference
27.3	20 min	Marigold	injury to leaves	Endress 1981
30.4	20 min	Spinach	injury to leaves	Endress 1981
13 to 27	20 min	Radishes; Pinto beans	visible foliar injury greater with higher temperature and greater amount of light	Granett 1981
not stated (gas)	20 min	Tomato and barley seeds	germination rate slightly reduced; suppression of seedling growth	Granett 1981
6 to 54.2	20 min	Pinto bean (8- to- 22-day-old seedlings)	Cl^- accumulated; 12-day-old plants accumulated less Cl^-	Endress 1979
6; 41.3	20 min	Pinto bean (8-day-old seedlings)	15% injury to leaves; 100% injury to leaves	Endress and Taylor 1979
29.7; 59.5	not stated	Corn	approx. 50% of total leaf area became necrotic; at 59.5 mg/m^3 reduced growth	Lind 1979

6.3.2.2 Plant studies. Some comments and conclusions gleaned from the literature are presented in this section. All data come from NAS (1976), unless specifically indicated otherwise. It was concluded by the very early work (work that is of questionable quality due to the lack of air circulation) that damage to vegetation, by the action of fumes containing hydrochloric acid on the soil or by influence of its reaction products in the ground, is not probable. Damage was afforded by direct action above ground. With respect to begonia, the damage was similar to that produced by hydrogen fluoride and sulphur dioxide. It was also apparent from the 1969 studies that the Bonny Best tomato was much more sensitive to hydrochloride gas than was the Neptune chrysanthemum. It was also concluded that the action of hydrogen chloride gas on the chlorophyll of the Bonny Best tomato is probably not due solely to the acidic properties of the gas.

Several studies were carried out involving morphology, histology, sensitivity factors that modify plant response, accumulation, and mimicking symptoms. These data are presented below:

Morphology (form and structure) of hydrogen chloride injury:

Rye - limp leaves appeared heavily bleached and shriveled, tannin deposits were visible in some cells in the vicinity of vascular bundles

Pea leaves - grains of chlorophyll appeared swollen, tannin deposits filled some cells

Roses - exhibited heavier tannin deposits than pea leaves

Montana pine - pale discoloration of the needles, browning and drying spreading from the tip

Spruce - red colouring of guard cells

Histology (tissue) of hydrogen chloride injury:

Tomato - underleaf surface glazing resulting from collapse of the lower epidermal cells

Tomato and chrysanthemum - bronzing appeared to result from the collapse of the lower epidermis, the spongy mesophyll and occasionally the palisade mesophyll and upper epidermis. It was concluded that the gas entered the plants through the stomata because tissues nearest the stomata were always first to be damaged. Substomatal injury closely resembles "dehydration" of cells lining the substomatal cavities of annual bluegrass damaged by smog. The bronzing symptom was similar to the "tan-coloured spot" symptom caused by hydrogen fluoride on apricot and by sulphur dioxide on pinto bean.

The order of tissue damage for tomato after entry of the gas through the stomata appears to be as follows:

- collapse of adjacent lower epidermal cells
- disorganization and collapse of the sponge mesophyll
- palisade mesophyll may or may not collapse, depending on severity of damage
- collapse of upper epidermis

It is concluded that tissue collapse in the chrysanthemum is not as severe as that in the tomato because the cell walls are thicker.

Factors that modify plant response to hydrogen chloride gas (tomato and chrysanthemum):

- Dose (concentration and length of fumigation)
- Relative frequency and abundance of stomata
- Relative humidity appears to be the dominant factor in symptom expression; the threshold above which injury will be severe and below which injury will be minimal for a given dose is as follows:
    - >80% - damage is typical of that caused by an acid (small discrete flecks on the exposed leaves)
    - <80% - damage is typical of that caused by a gas
- Cell wall thickness appears to influence severity of symptom expression
- Amount of intercellular space appears to influence severity of symptom expression
- Age of tissue appears to be important in symptom expression relative to the amount of chloride taken up by or translocated within the plants

Sensitivity of plants to hydrogen chloride gas:

- Broadleaf plants are generally more sensitive than coniferous plants

Accumulation of chloride in plants exposed to hydrogen chloride gas:

- Significant accumulation of chloride in all parts of tomato plants
- Actively growing tissues appear to have a greater tolerance for chloride than older leaves

Mimicking symptoms of plants exposed to hydrogen chloride gas:

- Glazing - first reported for peroxyacetylinitrate (PAN)
- Marginal leaf scorch resembles that caused by road salt ($NaCl$ or $Ca\,Cl_2$)

6.3.3 **Avian.** Exposure of pigeons to 150 mg/m^3 hydrogen chloride vapour for 6 hours daily for 50 days caused slight unrest and irritation of the eyes and nose; the hemoglobin concentration was only slightly diminished (Patty 1981).

6.4 Effect Studies

6.4.1 **Bacteria.** Gaseous hydrogen chloride in the presence of a minute of aerosol, rapidly inactivates bacterial spores of *Bacillus subtilis*, causing the spores to collapse (Lelieveld 1980). At ambient temperature and a pressure of 4 kPa (pressure of HCl over atmosphere pressure), naked spores of *B. subtilis* were reduced in viability by a factor of 100 000 within 10 seconds (Lelieveld and Van Eijk 1979).

6.4.2 pH Effects. In the aqueous environment, one measure of toxicity with respect to aquatic life is the pH or hydronium ion (H_3O^+) content. It is generally known that when the pH of a water body is rapidly lowered (hydronium ion concentration increased), such as would be the case with a spill of a large quantity of hydrogen chloride (liquid or aqueous solution) into the water body, a fish kill usually results. The extent of the overall damage would be influenced by the amount of acid, the buffering ability of the water, and the rate of dilution due to water flow. Extensive experimentation has been carried out with respect to acid deposition and its influence on water bodies, usually lakes. The acids usually associated with acid deposition are sulphuric and nitric, but the data regarding pH toxicity are thought to apply. In general terms, a pH lower than 5 is lethal to most fish (MHSSW 1976), although specialized aquatic flora and fauna may develop (WQC 1963). A very generalized summary of pH effects is shown below; more specific responses to low pH are shown in Section 6.4.2.2. The latter data are derived from studies involving the long-term problems associated with gradual acidification. All data are thought to be helpful in giving some insight into the aquatic environmental damage that may be caused by a spill of hydrogen chloride into a water body.

6.4.2.1 General summary of pH effects (WQC 1972).

pH	Effect
5.5-6.0	Eastern brook trout survive. Rainbow trout do not occur. Growth rate of carp is reduced. Spawning is reduced. Molluscs are rare.
5.0-5.5	Smaller populations of fish, but not lethal. May be lethal to eggs or larvae and some invertebrates. Algae and higher plants will grow.
4.5-5.0	No viable fishery can be maintained. Likely to be lethal to eggs and fry. Harmful to carp. Lethal to some invertebrates.
4.0-4.5	Only a few fish species survive. Only pike reproduce.

pH	Effect
3.5-4.0	All flora and fauna severely restricted.
3.0-3.5	Unlikely that any fish survive more than a few hours.

6.4.2.2 **Physiological responses to low pH.** Tolerance of low pH has been determined for several species of fish. For example, brook trout appear to be relatively acid-tolerant; very limited studies have shown this tolerance to be hereditary. A summary of pH effects is shown below (NRCC 1981):

Species	pH	Effect
Brook trout	2.5-3.25	Survival directly related to size and inversely to temperature
	3.0-3.5	Reduction in blood pH and loss of 50% of body sodium
	3.0-4.9	Sodium influx fell to zero, efflux increased, although sodium loss not believed to be cause of death
	4.0	Inhibition of RNA synthesis in intrarenal tissue
	4.5-4.8	Lower tolerance limit
	4.75-6.0	Reduced plasma sodium and chloride levels at lower pH
	low pH/4 days	Reduced oxygen tension in venous blood
Brook trout, spawning	4.0-4.5	Avoided the water with this pH range
Brook trout, young	<5.2	Tissue and cellular derangements including hypertrophy of mucous cells of gills, nares, skin; increased mucus secretion and epithelial necrosis of gills, corneas and skin

Species	pH	Effect
Brook trout, eggs	4.6-8.0	76 - 91% survival
	5.0	Significant reduction in viable eggs
	<6.5	Hatchability, growth reduced
Trout (no further ID)	4	Reduced plasma sodium and chloride levels (river in southern Norway)
Goldfish	3.0-4.9	Same results as for brook trout at similar pH
Brown trout	range of pH and electrolyte conc.	Measured electrical conductance across gills and concluded gill membrane was highly permeable to hydrogen ion; at low pH, a positive potential across gills resulted in a greater loss of sodium
Brown trout, eggs	4.5	Critical pH
Fathead minnow	4.2	Survived
	up to 5.2	Abnormal behaviour, deformed
	6.6	Safe for continuous exposure, marginal for vital life functions (embryo survival)
	6.5 down to 5.6	Disappeared from acidified lake
Fathead minnow, eggs	5.9	Hatchability and production reduced
Atlantic salmon, embryos	~3.6	Lower lethal limit during early cleavage
	3.9	LC_{50}
Atlantic salmon, older embryos	~3.0	Lower lethal limit during early cleavage
Atlantic salmon, alevins	~4.0	Lower lethal limit during early cleavage
	4.3	LC_{50}

Species	pH	Effect
Atlantic salmon, eggs	4.0	Hatching blocked
	4.5	Hatching delayed 15 days
	5.0-5.5	Critical pH
	7.0	Hatching delayed 7 days
Rainbow trout	4.0	Significant gradual decrease in pH and total CO_2 of blood of cannulated fish
	6 and 9	Oxygen consumption greater than at pH 7
Rainbow trout, embryos	4.75/10°C	Median lethal pH value
	5.52/5°C	Median lethal pH value
Rainbow trout, fingerlings	3.86-4.49	Median lethal pH value, related to temperature
Desert pupfish	5.0	Egg production ceased
	7.0 to 5.0	Egg production reduced
	6.5	Egg viability was 50% of that of control fish
Zebra fish, eggs	4	4% hatching success
	7	50% hatching success
White sucker, eggs	5.0	Incubated at pH 4.5 showed reduced survival and deformities
Perch, eggs	4.5	Sporadic hatching
	4.5-5.0	Prolonged non-hatching period of 5-10 days, malformed larvae
	<5.5	Reduced hatchability
Sea trout, eggs	4.5-5.0	Critical pH
Arctic char, eggs	4.5 - 5.0	Critical pH
Medaka	5	15% enzyme activity

Species	pH	Effect
Medaka, alevins	4.1	Many died in partly hatched state after incubation at pH 4.1
Pike, fry	4.2	Newly hatched, 97% mortality
	5.0	Newly hatched, 26% mortality
	6.8	Newly hatched, 17% mortality

General comments regarding early life history are provided. Teleost eggs shed into water quickly take up water into the perivitelline space between the ooplasmic and outer membranes. This process is known as water hardening and is accompanied by an increase in resistance to mechanical damage. Eggs deposited in acidic water will thus take up hydrogen ions, even in the hardened state. The effects are noted in the above table; however, the notable effects are delayed and/or impaired hatching and reduced survivability. Larval fish, post-hatching, may be the most acid-susceptible stage of the life history. Acclimation of embryos or larvae to acidity appears doubtful, with the possible exception of the brook trout.

6.5 Long-term Fate and Effects

Studies have been carried out regarding the effects of pH on acidic deposition in aquatic systems. These long-term (chronic) effects, although not necessarily related to the acute effects of a spill situation, are considered relevant to this manual since they may lead to a better understanding of the effects of pH. Increased hydrogen ion in an aquatic system may influence its geochemistry and biology over a period of time. The dynamics of water flow within the hydrological cycle influence the nature and extent of the geochemical and biological reactions. In particular, the time frames for these interactions are determined by the water flow, which governs the contact and residence times of the interacting materials. The geochemical aspects of the action of hydrogen ions on the surface components of the system involve both exchange reactions and mineral dissolution. Additional interactions of importance involve those with major lithologic elements such as Al^{+3}, Fe^{+3}, Mn^{+2} and certain trace metals. Hydrogen ions may also influence the biological cycling processes. The degree of sensitivity of aquatic ecosystems to acidification by external loading of hydrogen ions is determined by the base saturation component of the total exchange capacity and by the direct buffering capacity within the hydrologic system in question. The soils of certain parts of Canada are generally susceptible to acidic interaction with damaging effects. These soils are of glacial origin and contain unstable, fine-grained components which could release toxic metals or other elements to the groundwater or biologic systems by interaction with hydrogen ions (NRCC 1981).

In one particular experiment involving a lake in northwestern Ontario, the lake has been progressively acidified since 1976 by direct additions of sulphuric acid. The acid is added just after ice-out (May) to a preselected pH value. The pH is maintained throughout the ice-free season. The pH has been decreased from about 6.4 in 1976 to 5.6 in 1979. The changes in the biota of the lake are as follows:

Microorganisms - Decomposition, as measured by the rate of dissolved inorganic carbon generated in the hypolimnion or under winter ice, has not decreased, although a high proportion of it may be carried out by sulphate reducers.

Phytoplankton - There has been no evidence of oligotrophication (a process whereby an aquatic environment becomes more oligotrophic, i.e., one with a relatively low nutrient supply). Phytoplankton biomass has decreased slightly. Diatoms have all but disappeared and green algae have increased. The original phytoplakton species have been replaced by other more acid-tolerant ones.

Invertebrates - *Mysis relicta*, a major item in the diet of lake trout, almost disappeared at pH 5.8 during the winter. The exoskeleton of crayfish *(Orconectes virilis)* failed to harden after molting during a summer at pH 5.84. Both *Mysis* and *Orconectes* appear to have difficulty in recalcification after molting in waters of pH 5.5 to 5.7. Uptake of ^{45}Ca by crayfish was inhibited below pH 5.75 and ceased at pH 4.0.

Fish - Lake trout *(Salvelinus namaycush)* and white sucker *(Catastomus commersoni)* have maintained viable populations and normal spawning behaviour at pH levels as low as 5.5. However, there is evidence of increased incidence of embryonic mortality and deformity in the former species at pH 5.8 to 6.0. The growth rate and condition factor of larger fish have remained constant. Fathead minnows *(Pimephales promelas)* were no longer found following a pH reduction to 5.6.

The above data suggest that physiological mechanisms involved in calcification, egg formation and embryogenesis may be more important in the disappearance of aquatic animals than food chain effects due to lowered productivity of the system (NRCC 1981).

Hydrochloric acid may be neutralized slowly by natural alkalinity and dissolved carbon dioxide in water (OHM-TADS 1981) or by addition of neutralizing agents such as calcium carbonate ($CaCO_3$) or calcium hydroxide ($Ca(OH)_2$). There is evidence this process can partially reverse the damaging effects of chronic acidification and contamination by toxic metals (NRCC 1981) and can certainly increase the pH due to a spill, thereby minimizing the damage to the aquatic system.

6.6 Other Effects

6.6.1 Possible Effects on Water Treatment Plants. Hydrochloric acid may prevent coagulation by some agents through pH reduction (OHM-TADS 1981).

7 HUMAN HEALTH

Anhydrous hydrogen chloride is a colourless, corrosive, nonflammable gas with a characteristic pungent, suffocating odour. It is a respiratory irritant when in air. Airborne hydrogen chloride exists in the anhydrous (vapour) state and as an aerosol, i.e., as microdroplets of a solution of the gas dissolved in water. The anhydrous gas is highly hygroscopic; because of this characteristic, exposures to the vapour are potentially more dangerous to the biologic system than exposures to the hydrochloric acid aerosols. The vapour not only attacks by corrosive action, similar to the acid, but also by desiccation. Its affinity for water, however, makes general environmental chronic exposures to low concentrations of the anhydrous gas unlikely; acute exposure due to an emergency situation is, however, quite possible. Anhydrous hydrogen chloride readily fumes in atmospheric humidity and forms the aerosol. It should therefore be assumed that data from published reports regarding airborne hydrogen chloride pertain to the aerosol (hydrochloric acid) and not the vapour (anhydrous hydrogen chloride) unless specifically stated otherwise. Generally, exposures to the vapour are limited to the external surface of the body (integument and conjunctiva) and the lining of the respiratory tract (teeth and mucous membranes of the mouth, nose, pharynx, trachea, etc.). Contact with liquid anhydrous hydrogen chloride will cause severe burns due to the low temperature of the liquid and vaporization process, as well as severe tissue irritation and necrosis. Contact of concentrated hydrochloric acid with the skin can cause chemical burns or dermatitis. Ingestion is usually not a problem, since hydrochloric acid is a normal constituent of digestive juices (NAS 1976; Kirk-Othmer 1980; Matheson 1980).

The mechanisms of action of hydrogen chloride may be conveniently described in two parts - molecular and elementary biochemical effects, and disturbed function. The former mechanism involves the various potential reactions of the hydronium ion (H_3O^+) with the organic molecules of the mammalian system. As is readily known, hydrogen chloride, up to concentrations of 72 percent by weight at 20°C, is extremely soluble in water. It dissociates almost completely in the aqueous environment with the formation of hydronium and chloride ions:

$$HCl + H_2O \quad H_3O^+ + Cl^-$$

In this mechanism, the proton (H^+) is attached to the water molecule by a coordinate covalent bond with the charged species becoming a potential proton donor. Some possible reactions involve cleavage of organic molecules by virtue of the catalytic property of protons, as well as hydrolysis of peptides and of esters (both are cellular wall components), hydroxylation of carbonyl groups, and polymerization and depolymerization of organic molecules. With the loss of membrane integrity, the injured cell can readily be depleted of cytoplasmic components; cellular death may follow rapidly (NAS 1976).

With respect to the latter mechanism (disturbed function), necrosis (cellular death) is the most serious functional effect of acid burn. Erythema and edema usually precede it, with the latter the most characteristic manifestation. Edema occurs in any tissue that bears the brunt of the exposure. Edema of the cornea and conjunctiva, skin and surface mucosae, and deep respiratory tissues has been described in conjunction with substantial or massive exposures (NAS 1976).

Experiments with rodents suggest a discrepancy between animal species with regard to hydrogen chloride toxicity. For example, concentrations that effectively kill mice, guinea pigs and rabbits are not necessarily lethal to rats. Respiratory injury is the principal cause of death, with emphysema, atelectasis and pulmonary edema reflecting the extent of the damage. Residual alveolar injury may persist in animals sacrificed 14 days after exposure. Differences in severity or type of injury have not been detected between the aerosol and vapour phases of hydrogen chloride. The environmental temperature appears to be of some importance, as morbidity and mortality are higher at 37°C than at 20°C (NAS 1976).

No carcinogenic, mutagenic or teratogenic effects of exposure to gaseous hydrogen chloride have been reported (NAS 1976). Hydrogen chloride has been reported in the USEPA TSCA Inventory.

7.1 Recommended Exposure Limits

The exposure standards for hydrogen chloride/hydrochloric acid are based upon its toxic injury potential, but the level of exposure permitted by the standard is considered to be of borderline effectiveness in preventing severe irritation (Doc. TLV 1981). Canadian provincial guidelines are generally similar to those of USA-ACGIH, unless otherwise indicated.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV® (8 h)	USA-ACGIH	5 ppm (7 mg/m^3) (ceiling)	TLV 1983

Guideline (Time)	Origin	Recommended Level	Reference
PEL (10 h) (ceiling)	USA-OSHA	5 ppm (7 mg/m^3)	NIOSH Guide 1978
PEL (10 min)	USA-NRCC*	7 ppm (10 mg/m^3)	NAS 1976
PEL (30 min)	USA-NRCC*	3 ppm (5 mg/m^3)	NAS 1976
PEL (60 min)	USA-NRCC*	3 ppm (5 mg/m^3)	NAS 1976
Action Level	USA-OSHA	2.5 ppm (3.5 mg/m^3)	GE 1977
MAC	USSR	4 ppm	Doc. TLV 1981
MAC	West Germany	4 ppm	Doc. TLV 1981
MAC	Czeckoslovakia	5 ppm	Doc. TLV 1981

* National Research Council Committee on Toxicity Data (1971).

Short-term Exposure Limits (STEL)

A formal STEL has not been assigned as the 5 ppm limit is also a ceiling value which, as it applies to workplace situations, is not to be exceeded at any time. Some values have been proposed by the U.S. National Research Council Committee on Toxicology (NAS 1976).

Guideline (Time)	Origin	Recommended Level	Reference
Short-term Exposure Limits to Hydrogen Chloride			
STEL (10 min)	USA-NRCC Tox.	4 ppm (6 mg/m^3)	NAS 1976
(30 min)	USA-NRCC Tox.	2 ppm (3 mg/m^3)	NAS 1976
(60 min)	USA-NRCC Tox.	2 ppm (3 mg/m^3)	NAS 1976
(1 h/d)	USA-NRCC Tox.	2 ppm (3 mg/m^3)	NAS 1976
(5 h/d) (3-4 d/mo)	USA-NRCC Tox.	0.7 ppm (1 mg/m^3)	NAS 1976
Other Human Toxicities			
LC_{LO} (HCl aq., inhalation)		1300 ppm (30 min)	RTECS 1979
IDLH		100 ppm (anhydrons)	NIOSH Guide 1978
LC_{LO} (HCl anhy., inhalation)		1000 ppm (1 min)	RTECS 1979
LD_{LO} (HCl, aq., unknown route)		81 mg/kg	RTECS 1979

Guideline (Time) Origin	Recommended Level	Reference
Optical chronaxy reflex threshold concentration	0.402 ppm	NAS 1976
Digitovascular toxicity threshold concentration	0.335 ppm	NAS 1976
Threshold concentration for reflex effect on eye sensitivity to light	0.134 ppm	NAS 1976
Threshold concentration for change in rhythm and depth of respiratory movement	0.067 to 134 ppm	NAS 1976

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV, in ppm)

ITI = 1315.12 (31 580 mm Hg @ 20°C (for HCl (gas))/5)

ITI = 8.3×10^6

Because the ITI is a measure of vapour toxicity, it cannot accommodate information pertaining to the toxicity of dusts, solids or aerosols. It should be noted that a release of anhydrous hydrogen chloride will be converted to an aerosol by reaction with atmospheric moisture under most environmental conditions.

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
High concentrations of acid in water	Produces burns, ulceration, and scarring on skin and mucous membranes	USDHEW 1977
High concentrations of acid	May cause dermatitis and photosensitization	TDB (on-line) 1981

Exposure Level (and Duration)	Effects	Reference
1 N HCl (120 min)	Minimum exposure for damage to tissue to be microscopically evident	NAS 1976

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
High concentration	Causes eye irritation and may cause prolonged or permanent visual impairment including loss of vision	NIOSH/OSHA 1981

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristic: Sharp, pungent irritating (AAR 1981). Odour Index: 29 928 (AAR 1981).

Parameter	Media	Concentration	Reference
Odour Threshold (Russian)	In air	0.2 mg/m^3 (0.13 ppm)	NAS 1976
Odour Threshold	In air	1 to 5 ppm	AAR 1981
Odour Threshold	-	10 ppm	NAS 1976
Odour Threshold (Russian)	Aerosol	0.1 mg/m^3 (0.067 ppm)	NAS 1976
Odour Threshold (Russian)	In air	0.39 mg/m^3 (0.26 ppm)	NAS 1976
Upper Recognition Threshold	In air	5 ppm	AAR 1981
Recognition	In air	10 ppm	ASTM 1980
Lower Odour Threshold	-	1 ppm	OHM-TADS 1981
Upper Odour Threshold	-	5 ppm	OHM-TADS 1981

As can be seen, the odour threshold range from the various references is 0.067 to 10 ppm hydrogen chloride (aerosol) in air. This compares favourably to a subjective response study involving trained industrial hygienists as shown below (NAS 1976):

Response	No. Observations	Hydrogen Chloride Concentration (ppm)	
		Average	Range
None	6	0.4	0.06 - 1.8
Minimal	4	0.7	0.07 - 2.17
Easily noticed	5	4.17	1.9 - 8.6
Strong	5	13.37	5.6 - 22.1

7.3.2 **Taste.** Taste Characteristic: Sour, chlorine-like (AAR 1981).

Parameter	Media	Concentration	Reference
Recognition Taste Threshold	In water	16 millimoles/Litre	ASTM 1980
Recognition Taste Threshold	In water	18 millimoles/Litre	ASTM 1980
Recognition Taste Threshold	In water	11 millimoles/Litre	ASTM 1980
Recognition Taste Threshold	In water	9.0×10^{-4} N	ASTM 1980
Recognition Taste Threshold	In water	31 mg/100 mL	ASTM 1980
Recognition Taste Threshold	In water	50 millimoles/Litre	ASTM 1980
Median Taste Threshold	-	32 ppm	OHM-TADS 1981

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
2000 to 1300 ppm (few minutes)	Death	NAS 1976
1300 ppm (30 min)	LC_{L0} (Hydrochloric acid)	RTECS 1979
1000 ppm (1 min)	LC_{L0} (Hydrogen chloride)	RTECS 1979
100 to 500 ppm (60 min)	Intolerable	NAS 1976
100 to 50 ppm	Work impossible	NAS 1976
50 to 10 ppm	Work difficult but possible	NAS 1976
35 ppm	Irritation of the throat after short exposure	NAS 1976
10 ppm	Irritation	NAS 1976
10 ppm	Work undisturbed	NAS 1976
5 ppm	No organic damage	NAS 1976
SPECIES: Mammalian (unspecified)		
1000 mg/m^3 (2 h)	LC_{L0} (HCl anhyd.)	ITII 1981; RTECS 1979
SPECIES: Cat		
5000 mg/m^3 (1 1/2 h)	Death after 2 to 3 days	NAS 1976
2000 mg/m^3 (2 to 6 h)	Caused severe irritation, dyspnea, and clouding of the cornea	Patty 1981
1000 mg/m^3 (2 to 6 h)	Some fatalities	Patty 1981
210 to 150 mg/m^3 (up to 360 min) (HCl vapour)	Salivation, rhinorrhea, no sequelae	NAS 1976

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
6500 mg/m^3 (30 min) (HCl vapour)	100% deaths. Fairly resistant to immediate effects of hydrogen chloride, but died later from pulmonary or nasal infections. Liver lesions noted in 1/3 of the rabbits	NAS 1976
6400 mg/m^3 (30 min)	LC$_{50}$	RTECS 1979
5500 mg/m^3 (5 min)	No deaths (vapour)	NAS 1976
5000 mg/m^3 (90 min)	Death 2 to 6 days after exposure (vapour)	NAS 1976
2000 mg/m^3 (75 min)	Severe irritation, dyspnea and clouding of the cornea. Some fatalities	Patty 1981
2000 mg/m^3 (75 min)	Respiratory distress, corneal opacity (vapour)	NAS 1976
1000 mg/m^3 (90 to 360 min)	100% deaths (vapour)	NAS 1976
450 mg/m^3 (360 min)	Cloudy cornea and catarrh (vapour)	NAS 1976
150 to 210 mg/m^3 (up to 360 min)	Salivation, rhinorrhea (vapour)	NAS 1976
90 mg/m^3 (5 min), 45 mg/m^3 (10 min)	Ciliary activity in the excised tissue ceased without recovery (vapour)	Patty 1981
4416 ppm (30 min)	LC$_{L0}$ (anhydrous)	RTECS 1979
SPECIES: Rat		
60 100 mg/m^3 (5 min)	LC$_{50}$ (vapour)	NAS 1976
48 507 mg/m^3 (5 min)	Lowest concentration causing death (vapour)	NAS 1976
47 500 mg/m^3 (5 min)	Lowest dose causing death (237 500 mg-min/m^3)	NAS 1976
45 600 mg/m^3 (5 min)	LC$_{50}$ (aerosol)	NAS 1976
8300 mg/m^3 (30 min)	LC$_{50}$ (aerosol)	NAS 1976

Exposure Level (and Duration)	Effects	Reference
6900 mg/m^3 (30 min)	LC$_{50}$ (vapour)	NAS 1976
6900 mg/m^3 (127 500 mg-min/m^3 (30 min)	LCt$_{50}$* (vapour)	NAS 1976
28 775 mg/m^3 (5 min)	Lowest concentration causing death (aerosol)	NAS 1976
4336 mg/m^3 (30 min)	Lowest concentration causing death (aerosol)	NAS 1976
3990 mg/m^3 (30 min)	Lowest concentration causing death (vapour)	NAS 1976
3124 ppm (1 h)	LC$_{50}$ (HCl aq.)	RTECS 1979
SPECIES: Mouse		
20 200 mg/m^3 (5 min)	LCt$_{50}$* (101 000 mg-min/m^3) (vapour)	NAS 1976
16 500 mg/m^3 (5 min)	LC$_{50}$ (aerosol)	NAS 1976
13 496 mg/m^3 (5 min)	Lowest concentration causing death (aerosol)	NAS 1976
52 800 mg-min/m^3 (30 min)	Lowest concentration causing death (vapour)	NAS 1976
4768 mg/m^3 (5 min)	Lowest concentration causing death (vapour)	NAS 1976
4750 mg/m^3 (5 min)	Lowest dose causing death	NAS 1976
3900 mg/m^3	LC$_{50}$ (vapour)	NAS 1976
3870 mg/m^3 (30 min)	LCt$_{50}$* (116 100 mg-min/m^3) (vapour)	NAS 1976
3100 mg/m^3 (30 min)	LC$_{50}$ (aerosol)	AAR 1981
1794 mg/m^3 (30 min)	Lowest concentration causing death (vapour)	NAS 1976
1690 mg/m^3 (30 min)	Lowest concentration causing death (aerosol)	NAS 1976
SPECIES: Guinea Pig		
5500 mg/m^3 (5 min)	No deaths (HCl vapour)	NAS 1976

* LCt = Lethal Concentration in mg-min/m^3

Exposure Level (and Duration)	Effects	Reference
5000 mg/m^3 (90 min)	Death 2-6 days after exposure (HCl vapour)	NAS 1976
2000 mg/m^3 (75 min)	Respiratory irritation, corneal opacity (HCl vapour)	NAS 1976
1000 mg/m^3 (360 min)	100% deaths (HCl vapour)	NAS 1976
450 mg/m^3 (360 min)	Cloudy cornea, catarrh (HCl vapour)	NAS 1976
6500 mg/m^3 (30 min)	100% deaths (HCl vapour)	NAS 1976
Chronic Exposures		
SPECIES: Human		
Not specified (3 mo)	Earliest etching of tooth enamel in plant workers	NAS 1976
Not specified (18 mo)	Earliest erosion of tooth enamel in plant workers	NAS 1976
Not specified (6 yr)	Earliest erosion to expose secondary dentin in plant workers	NAS 1976
SPECIES: Rabbit		
150 mg/m^3 (360 min/d for 50 d)	Unrest, irritation of eyes and nose (HCl vapour)	NAS 1976
100 mg/m^3 (360 min/d for 5 d)	Inflammatory reaction in respiratory tract (HCl vapour)	NAS 1976
50 mg/m^3 (360 min/d for 20 d)	No effects, no pathology (HCl vapour)	NAS 1976
SPECIES: Guinea pig		
150 mg/m^3 (360 min/d for 50 d)	Unrest, irritation of eyes and nose (HCl vapour)	NAS 1976
100 mg/m^3 (360 min/d for 5 d)	Inflammatory reaction in respiratory tract (HCl vapour)	NAS 1976
50 mg/m^3 (360 min/d for 20 d)	No effects, no pathology (HCl vapour)	NAS 1976
SPECIES: Monkey		
50 mg/m^3 (360 min/d for 20 d)	No effects, no pathology (HCl vapour)	NAS 1976

Guinea pig deaths were attributed to acute respiratory damage. High concentrations caused necrosis of the trachea and bronchi, edema, atelectasis, emphysema and damage to pulmonary blood vessels. Gross pathologic changes were noted in the livers of 79 percent of the guinea pigs that died; pulmonary lesions were noted in those that died or were sacrificed between 1 and 18 months after exposure. Rabbits were more resistant to the immediate effects of hydrogen chloride vapour, but died later from pulmonary or nasal infections. Severe lesions were noted in the livers of 31 percent of the rabbits that died. The 50-day tests resulted in only slight unrest and irritation of the eyes and nose in both rabbits and guinea pigs (NAS 1976).

Mice appear to be more sensitive to the lethal effects of hydrogen chloride vapour than are rats, guinea pigs, rabbits or monkeys. Within a given species, the degree of damage is related to the Ct over the known ranges of concentration and exposure. The LCt_{50} for mice is about half that for rats. Data indicate that irreversible toxic effects or death will occur only rarely after single exposures of 5 min or more at a Ct of 10 000 mg-min/m^3 or less, even in mice. The LCt_{50} is about 100 000 mg-min/m^3 for mice and about 250 000 mg-min/m^3 for rats for exposure times of 5 or 30 min. Clouding of the cornea occurs at LCt_{50} in rabbits and guinea pigs. It was shown that irritation, salivation and rhinorrhea occur at a Ct of about 50 000 mg-min/m^3 in rabbits and guinea pigs; daily Cts of 18 000 mg-min/m^3 (50 mg/m^3 for 6 h/d) for 20 days do not produce any signs of irritation or morphology (even in monkeys). Generally speaking, however, there are few published data on the effects of inhaled hydrogen chloride on the various body organs or systems of animals (NAS 1976).

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
900 mg/kg	LD_{50} (HCl aq.)	OHM-TADS 1981

7.4.3 Intraperitoneal.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
40 mg/kg	LD_{50} (HCl aq.)	OHM-TADS 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

In man, the effects of exposure to hydrogen chloride vapour or aerosol are usually confined to inflammation and possibly ulceration of the nose, throat and larynx; laryngeal spasm or pulmonary edema occur on rare occasions. Eye and skin burns have been observed at higher concentrations, but contact must be for extended periods. Rapid flushing with copious amounts of water will usually prevent serious damage. The latter applies to vapour, aerosol or solution. Vapour dissolved in perspiration may cause dermatitis. Etching and/or erosion of the front teeth may occur with exposure to gaseous hydrogen chloride, although dental caries are not apparently increased. It was noted that no significant abnormalities have been associated with chronic exposures to low concentrations of gaseous hydrogen chloride, i.e., no pulmonary-function changes were observed in those chronically exposed, whereas acute exposure to similar concentrations did produce the symptoms. Acclimation is suggested (NAS 1976).

7.5.1 Inhalation (Vapour/aerosol).

1. Irritation of the nose, throat and eyes. (May cause bleeding of the nose and gums.)
2. Irritation and inflammation of the upper respiratory tract.
3. Headache.
4. Laryngeal spasms.
5. Laryngitis (ITII 1981).
6. Coughing and choking.
7. Ulceration of the oral and nasal mucosa.

8. Erosion and etching of the teeth.
9. Bronchitis (ITII 1981).
10. Pneumonia (ITII 1981).
11. Nasoseptic perforation (ITII 1981).
12. Pulmonary edema (under severe exposure conditions).
13. Palpitations (ITII 1981).
14. Death (NAS 1976).

7.5.2 **Ingestion** (Hydrochloric acid).

1. Salivation.
2. Intense thirst.
3. Irritation and burning sensation of lips and throat.
4. Burning sensation at the esophagus, back of throat, and stomach.
5. Pain in swallowing.
6. Severe burns of the mucous membranes of the mouth, esophagus and stomach.
7. Lips and mouth usually turn white and later brown (MCA 1970).
8. Edema of the glottis.
9. Nausea and vomiting, occasionally of blood.
10. Diarrhea (MCA 1970).
11. Difficulty in breathing.
12. Risk of perforation of the stomach.
13. Nephritis (ITII 1981).
14. State of shock.
15. Convulsions.
16. Coma.
17. Death (MCA 1970).

7.5.3 **Skin Contact** (Vapour, aerosol or aqueous).

1. Smarting.
2. Burning sensation.
3. Inflammation.
4. Burns that may be very painful and become white (Lefèvre 1980).
5. Painful blisters.
6. Dermatitis (MCA 1970).
7. Profound damage to tissues.

7.5.4 **Eye Contact** (Vapour/aerosol).

1. Watering of eyes.
2. Stinging or burning sensation with ulcerations.
3. Conjunctivitis (Lefèvre 1980).
4. Photosensitization (TDB (on-line) 1981).
5. Opaqueness of the cornea (Lefèvre 1980).
6. Corneal necrosis.

7.6 Human Toxicity to Decay or Combustion Products

When subjected to heat, hydrogen chloride is a stable gas but is slightly dissociated, at high temperature, into H_2 and Cl_2 (Partington 1968).

7.6.1 **Hydrogen and Chlorine.** Hydrogen is a colourless, odourless, tasteless gas which, when mixed with air, forms explosive mixtures. With air and an ignition source, the air-gas mixture burns.

Chlorine is a greenish-yellow diatomic gas with a suffocating odour. This gas is a powerful irritant and can cause fatal pulmonary edema if inhaled. Other symptoms include respiratory complaints, corrosion of the teeth, inflammation of the mucous membranes of the nose and increased susceptibility to tuberculosis in workers chronically exposed. The TLV® for chlorine is 1 ppm and the STEL is 3 ppm (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Hydrogen Chloride with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Water							●						Produces toxic and corrosive fumes (HCl aerosol)	Sax 1979
SPECIFIC CHEMICALS														
Calcium Carbide		●										●	Reacts with incandescence	NFPA 1978
Cesium Acetylene Carbide		●											Cesium acetylene carbide burns in hydrogen chloride gas	NFPA 1978
Dowicil 100 (anti-microbial agent)						●							Immediate decomposition	NFPA 1978
Fluorine		●											Gases incandesce	Bretherick 1979
Lithium Silicide		●											Incandesces	NFPA 1978
Mercuric Sulphate											●		Violent absorption above 125°C	NFPA 1978
Sodium											●		On contact	NFPA 1978

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Hydrogen Chloride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
CHEMICAL GROUPS														
Metal Acetylides (carbides)		●											Ignite or incandesce	Bretherick 1979

8.2 Compatibility of Hydrochloric Acid with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
SPECIFIC CHEMICALS														
Acetic Anhydride													With 36% acid, heat generated in closed vessel	Bretherick 1979; NFPA 1978
Aluminum Powder													With 36% acid in closed container	NFPA 1978
2-Aminoethanol														NFPA 1978
Aqueous Ammonia													Acid and 28% ammonia solution	NFPA 1978
Calcium Phosphide													With acid	NFPA 1978
Cesium Carbide													Ignites with strong acids	NFPA 1978
Chlorosulphonic Acid													With 36% HCl acid in closed container	NFPA 1978
Ethylene Diamine													With 36% HCl acid in closed container	NFPA 1978
Ethylenimine													With 36% acid	NFPA 1978

8.2 Compatibility of Hydrochloric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Fluorine		●											Incandesces in contact with strong acids	Bretherick 1979
Hexalithium Disilicide				●									In dilute acid, evolves silicon hydrides which ignite; incandesces in dilute solutions	Bretherick 1979
Lithium Silicide				●									Produces spontaneously flammable gas	NFPA 1978
Magnesium Boride				●									Produces spontaneously flammable gas	NFPA 1978
Oleum	●												Decomposes spontaneously and violently	NFPA 1978
Perchloric Acid						●			●		●		With 36% acid	NFPA 1978
Potassium Permanganate		●											With concentrated acid and contamination (possibly sulphuric acid)	Bretherick 1979

8.2 Compatibility of Hydrochloric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Propiolactone (Beta)	●								●				With 36% acid	NFPA 1978
Propylene Oxide	●								●				In a closed container	NFPA 1978
Silicon Dioxide	●													Bretherick 1979
Silver Perchlorate			●										With acid and carbon tetrachloride, produces trichloromethyl perchlorate which detonates at 40°C	NFPA 1978
Sodium			●										Explodes on contact	Bretherick 1979
Sodium Hydroxide	●								●				With 36% acid	NFPA 1978
Sulphuric Acid			●						●				Dehydration reaction, could be violent in large quantities	Bretherick 1979
Rubidium Acetylide		●											Burns with warm acid	NFPA 1978
Rubidium Carbide		●											Ignites with strong acid	NFPA 1978

8.2 Compatibility of Hydrochloric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Tetraselenium Tetranitride			●										Explosive with fuming hydrochloric acid	Bretherick 1979
Uranium Phosphide				●									Releases a spontaneously flammable phosphine	NFPA 1978
Vinyl Acetate	●								●				With 36% acid	NFPA 1978
CHEMICAL GROUPS														
Alcohols & Glycols	●												Dehydration reaction	EPA 600/2-80-076
Aldehydes	●				●									EPA 600/2-80-076
Amines	●												Forms ammonium salts	EPA 600/2-80-076
Caustics	●										●			EPA 600/2-80-076
Epoxides	●				●									EPA 600/2-80-076

8.2 Compatibility of Hydrochloric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Esters	●					●							Causes hydrolysis or decomposition	EPA 600/2-80-076
Explosives	●		●										Heat may be sufficient to detonate	EPA 600/2-80-076
Flammable Compounds	●					●	●						As a strong oxidizer	EPA 600/2-80-076
Halogenated Organics	●					●	●							EPA 600/2-80-076
Ketones	●												Aldol condensation	EPA 600/2-80-076
Metals and Metal Complexes							●			●				EPA 600/2-80-076
Metal Acetylides (carbides)		●											Ignite in concentrated hydrochloric acid	Bretherick 1979
Oxidizing Agents	●						●						Yield toxic and corrosive chloride gases	EPA 600/2-80-076

8.2 Compatibility of Hydrochloric Acid with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Phenols and Cresols	●					●							Substitution or decomposition may occur	EPA 600/2-80-076
Reducing Agents	●	●		●									Yields hydrogen	EPA 600/2-80-076
Unsaturated Aliphatics	●													EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Hydrogen chloride is nonflammable and noncombustible (Air Products SGDS 1980). Hydrochloric acid, on contact with common metals, produces explosive and flammable hydrogen gas (NFPA 1978; GE 1977). Explosive concentrations of hydrogen may accumulate inside metal containers (Du Pont MSDS 1979).

9.1.2 Fire Extinguishing Agents. Use water spray to cool containers involved in a fire to help prevent rupture. Water spray may also be used to reduce vapours (ERG 1980; GE 1977). Move containers from fire area if this can be done without risk. Avoid adding water inside containers (ERG 1980; EAG 1978). Stay away from tank ends (EAG 1978). Water spray or fog is an effective means of cooling containers involved in a fire and of controlling the emission of gaseous hydrogen chloride. Water, however, should never be applied to a leaking container, as the hydrochloric acid formed at the leak site will always cause a more severe leak due to corrosion of the metal container. This situation is similar to that encountered with chlorine.

9.1.3 Evacuation. The following information consists of evacuation distances which appear in the literature. Important parameters such as spill quantities, concentration level to which evacuation is suggested, and environmental conditions, may not be defined. Readers are advised to evaluate the use of these values with those derived from the methods to calculate hazard zones in Section 5.3 of this manual, which uses the above data. The following are recommended evacuation distances from the immediate danger area of a spill, based on prevailing winds of 10 to 19 km/h (EAG 1978).

Approximate Size of Spill	Distance to Evacuate from Immediate Danger Area	For Maximum Safety, Downwind Evacuation Area Should be
20 m^2	115 m (150 paces)	810 m long, 810 m wide

Approximate Size of Spill	Distance to Evacuate from Immediate Danger Area	For Maximum Safety, Downwind Evacuation Area Should be
35 m^2	165 m (216 paces)	1620 m long, 810 m wide
55 m^2	205 m (270 paces)	1620 m long, 1620 m wide
75 m^2	240 m (312 paces)	2430 m long, 1620 m wide

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact with acid solutions and inhalation of vapours (GE 1977). If a leak in a container cannot be stopped, the container should be removed to the outdoors or to an isolated, well-ventilated area. The container should be placed in such a position that it will gradually lose its contents as a gas without damage or hazard. The gas should be exhausted into an absorption system containing water or an alkaline solution in such a manner that suck-back cannot occur (MCA 1970).

The following absorbent materials have been tested and recommended for vapour suppression and/or treatment of 26 and 35 percent HCl solutions (Braley 1980): a mixture of 75 percent anionic polyacrylamide (R 1779) and 25 percent nonionic polyacrylamide (Versicol W25), or use the following anionic polyacrylamide or nonionic polyacrylamide, and Cellosize WP3H (hydroxyethyl cellulose).

9.1.4.2 Spills on land. All spills involving liquid hydrogen chloride or hydrochloric acid should be contained, if possible, to prevent entry into bodies of water or sewer systems. Vapour from either form can be knocked down with water fog or spray. Liquid hydrogen chloride, if not recoverable, can be diluted with water to reduce vaporization; however, the dilution process will cause violent boiling which will necessitate continuous water fog to help control the aerosolization. Hydrochloric acid should be recovered, if possible. If recovery of the aqueous contaminant is not possible, the material should be neutralized with the appropriate agents to minimize side effects of environmental concern.

9.1.4.3 Spills in water. Spills of either liquid hydrogen chloride or hydrochloric acid into a water body will lower the pH of the water and increase the chloride content.

The area of contamination should be confined with barriers if possible and the pH brought back to the normal level of the uncontaminated water body.

9.1.5 Cleanup and Treatment.

9.1.5.1 Spills on land. For small spills of hydrochloric acid or diluted liquid hydrogen chloride, the contaminated area, aqueous solution or residual solid should be treated with soda ash (Na_2CO_3) or lime (CaO) until neutralization is afforded. The residue can then be shoveled into containers for disposal (GE 1977).

For large spills, the aqueous solution remaining (after recovery) or the entire spill should be neutralized cautiously with limestone ($CaCO_3$), lime (CaO) or soda ash (Na_2CO_3) (Dow MSDS 1979a,b). The residual sludge can be shoveled into containers for disposal. Application of fly ash or cement powder to absorb the aqueous contaminant can be considered (EPA 670/2-75-042). Activated carbon may also be used (CG-D-38-76).

9.1.5.2 Spill in water. The contaminated water body can be treated with sodium bicarbonate ($NaHCO_3$), an in situ neutralizing agent that will usually avoid overdosing, a situation that would increase the pH beyond that of the noncontaminated water body. Other treating agents to be considered are lime (CaO), limestone ($CaCO_3$) and soda ash (Na_2CO_3) (CD-D-16-77).

9.1.5.3 General. For treatment of contaminated water recovered from the spill site, gravity separation of solids followed by neutralization with a mixture of soda ash (Na_2CO_3) and lime (CaO) (50/50) is recommended. Stirring may be necessary to increase the reaction rate (EPA 600/2-77-227). Anion exchange is also recommended for neutralization (OHM-TADS 1981).

9.1.6 Disposal. Waste hydrochloric acid or acid-contaminated water must never be discharged directly into sewers or surface waters. Following neutralization, either at the spill site or at a waste management facility, the resultant sludge can be disposed of to a secure landfill. The water may be released to the environment provided that all environmental concerns have been met.

9.1.7 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be hydrogen chloride (in the anhydrous or aqueous form):

- Response personnel should be provided with and required to use impervious clothing, gloves, face shield (20 cm minimum), and other appropriate protective clothing necessary to prevent any possibility of repeated or prolonged skin contact with mists or solutions of hydrogen chloride. Splash-proof safety goggles are also recommended for eye protection (NIOSH/OSHA 1981).
- Woolen outside clothing has been recommended (GE 1977). PVA is not recommended for gloves (OHM-TADS 1981). Soft-brimmed hats or caps may be worn to give head protection against liquid leaks and splashes (MCA 1970). Plastic hard hats are recommended (PPG 1979).
- The following chemical suit materials are recommended for protection against hydrochloric acid (EE-20): Cloropel and PVC (excellent resistance) and neoprene (good resistance).
- Non-impervious clothing which becomes contaminated with solutions of hydrogen chloride should be removed immediately and not reworn until the hydrogen chloride is removed from the clothing (NIOSH/OSHA 1981).
- Eye wash fountains and instant-acting showers must be readily available in areas of use and spill situations (GE 1977).
- The following is a list of the minimum respiratory protection recommended for personnel working in areas where hydrogen chloride is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Gas Concentration 50 ppm or less	Any chemical cartridge respirator with an acid gas cartridge(s). Any supplied-air respirator. Any self-contained breathing apparatus.
100 ppm or less	Any chemical cartridge respirator with a full facepiece and an acid gas cartridge(s). A gas mask with a chin-style or a front- or back-mounted acid gas canister. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.

Condition	Minimum Respiratory Protection* Required Above 5 ppm
Greater than 100 ppm** or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases.
	Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

** Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of hydrogen chloride; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 100 ppm, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.

9.1.8 Storage Precautions. Store closed containers in clean, cool, open or well-ventilated areas. Keep out of sun. Area should have acid-resistant floor and approved drainage. Keep away from oxidizing agents and alkaline materials. Protect containers from damage or breakage. Use nonsparking tools in areas around tanks and pipes where hydrogen might be generated (GE 1977). Do not store or mix with cyanides, sulphides or formaldehydes (Du Pont MSDS 1979). No part of a cylinder should be subjected to a temperature above 52°C (Air Products MSDS 1978).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the reference study.

Leak Plugging	Plug N' Dike™
Treating Agents	Hazorb (sorbent)

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included; thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.1 **Storage Tank Spill** (Personal Communication with RCRI 1982; HMIR 1980)

A storage tank, containing about 750 000 L of 32 percent hydrochloric acid solution, started to leak its contents when the natural rubber protective lining of the tank deteriorated and the acid dissolved the flange at its base. Approximately 380 000 L of the hydrochloric acid solution spilled on the ground and flowed towards a nearby river before remedial actions were undertaken. A vapour cloud occurred above the spill and dissipated within 300 m of the spill site.

Fire fighters initially used water to wash the acid out of the spill area; however, this spill action was halted in order to reduce the amount of acid reaching the river. Response crews arrived at the spill site wearing protective clothing and filter masks. Fourteen truckloads of oyster shells were applied onto the spill area. The shells served a dual purpose: temporary containment of the acid (by building dams with the shells), and neutralization. The neutralized residue was then raked and shoveled into containers for disposal. The remaining hydrochloric acid in the leaking tank was transferred to another tank.

The acid that reached the river killed more than 20 fish and a few blue crabs. Water samples revealed no abnormal environmental effects since the river had been highly polluted for quite some time. Several response personnel developed facial rashes 2 or 3 days after the incident. This may have resulted when the winds suddenly shifted direction and increased the exposure of acid fumes to their faces.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water, and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI). Other references were reviewed where warranted.

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought. If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well. Commercially, the concentration of hydrochloric acid is commonly measured in terms of specific gravity of the solution. General practice in the laboratory, however, is to determine the concentration of aqueous hydrogen chloride volumetrically, e.g., by titration with standard base for hydronium ion concentration, or gravimetrically by precipitation of silver chloride. In fact, many other methods exist which include spectrophotometric, potentiometric, colourimetric, turbidimetric and polarographic. Complexity of the method will in fact determine the methods presented in this manual. In general practice, hydrogen chloride in the vapour aerosol phase, irrespective of concentration, is first trapped in a suitable medium, such as water, standard sodium hydroxide or sodium carbonate solutions, etc., and then analyzed by the method of choice. The absence of interfering materials should be verified by simple qualitative tests. Water and soil samples should be taken and handled according to standard laboratory procedures specific to hydrogen chloride. Noncontaminated samples taken from as close to the incident site as possible should be used as standards.

11.1 Quantitative Methods for the Detection of Hydrogen Chloride in Air

11.1.1 **Ion Specific Electrode** (NIOSH 1977). This method is useful over a range of 1 to 20 mg/m^3 (0.05 to 1.0 ppm) hydrogen chloride in air for 15 L samples. The range may be extended to include more concentrated samples by using smaller air sample volumes.

A known volume of air, approximately 15 L, is drawn through a midget bubbler containing 10 mL of 0.5 M sodium acetate solution. The sample is diluted to 25 mL with water and analyzed using a chloride ion specific electrode. This method is not specific for hydrogen chloride since any chloride will give positive interference. Sulphide ion must not be present since it poisons the electrode. The chloride ion level must be at least 3×10^2 times the bromide ion level, 2×10^6 the iodide ion level and 5×10^6 the cyanide ion level to avoid interference. High concentrations of species which form stable complexes with silver ion produce positive interference. The coefficient of variation is 0.064. This is a fast and accurate method.

11.1.2 **Colourimetric** (Leithe 1971). A range of 0.05 to 0.74 ppm hydrogen chloride in air may be analyzed by this method if air is sampled for 1 hour at 3 L/min. The air sample volume is adjusted to give between 10 and 200 µg chloride in a 50 mL reaction solution.

A known volume of air is drawn through 30 mL of 0.01 N sodium hydroxide at a rate of 3.0 L/min. The absorption liquid is transferred into a 250 mL volumetric flask. Two drops of 2 N nitric acid, 1 mL of a 1 percent solution of mercuric thiocyanate ($Hg(SCN)_2$) in methanol and 8 g of ferric ammonium sulphate ($FeNH_4(SO_4)_2$, ferric alum) in 100 mL of 6 N nitric acid are added. The solution is diluted to volume and the absorbance is measured at 460 nm in a spectrophotometer. Bromides, iodides, sulphides, thiosulphates, cyanides and nitrites interfere. The method is simple, does not require specialized equipment and is rapid. The method is not specific for hydrogen chloride; however, it will measure total chloride in a sample. The reaction type is a complex formation and involves the formation of mercuric chloride ($HgCl_2$), tetrachloromercurate ion ($HgCl_4$) and thiocyanate ion (SCN^-). The latter complexes with ferric ion (Fe^{+++}) to form a coloured solution (Leithe 1971; Bailar 1973).

11.2 Qualitative Method of Detection of Hydrogen Chloride in Air

The presence of hydrogen chloride can be qualitatively determined by simply detecting the presence of the chloride ion. The classical method in aqueous solution is accomplished by precipitating the sparingly soluble silver chloride in acidic solution. Another simple method is to carry out the procedure described in Section 11.1.2 but without the use of the spectrophotometer. The reddish-orange colour of the iron (III)-thiocyanate complex indicates the presence of chloride ion. Interfering ions will falsely indicate the presence of chloride ion. The original air sample can be collected by the methods described in Sections 11.1.1 or 11.1.2 or by any other technique such as absorber or impinger trains or in evacuated bulbs.

The silver chloride method is accomplished by adding a solution of silver nitrate ($AgNO_2$) to an acidified (with nitric acid) solution suspected of containing hydrogen chloride. The formation of a white precipitate, AgCl, indicates the presence of chloride ion. The other halide ions, Br^- and I^-, interfere; however the precipitates, AgBr and AgI, are coloured to some extent and can be easily distinguished from AgCl. In addition, silver chloride is more soluble in aqueous ammonia than is the bromide and iodide, with the formation of the complex ion $Ag(NH_3)_2^+$. It is therefore good practice to add aqueous ammonia to the acidified mixture with stirring until basic or to the solid - silver chloride will readily dissolve. Reprecipitation of the white solid will occur by adding nitric acid. Other ions that will interfere are sulphide and thiocyanate.

11.3 Quantitative Methods for the Detection of Hydrochloric Acid in Water

11.3.1 Colourimetric (ASTM 1979). Chloride concentrations ranging from 0.02 to 10 ppm in water may be determined. This method is similar to that described in Section 11.1.2.

Representative samples of at least 50 mL are collected in glass bottles. Ferric alum solution is prepared by dissolving 28 g of ferric ammonium sulphate (ferric alum) crystals in 80 mL of water, cool, filter and dilute to 100 mL with 6 N nitric acid. Mercuric thiocyanate solution is prepared by dissolving 0.30 g of mercuric thiocyanate in 100 mL of methanol and allowing the solution to stand for 24 hours. Five millilitres of ferric alum solution and 2.5 mL of mercuric thiocyanate solution are mixed with 25 mL of sample and allowed to stand for 10 minutes. The colour developed is measured on a spectrophotometer at 466 nm. Bromides, iodides, thiosulphates, cyanides, sulphides and nitrites interfere with the analysis. The method is sensitive, rapid, and easily adapted for automated analysis. The method is not specific for hydrogen chloride and will identify as chloride any ion that displaces thiocyanate.

11.3.2 Mercuric Nitrate Titration (AWWA 1976). This method is suitable for the detection of a range of 3 to 200 ppm chloride in water. This is equivalent to 0.15 to 10 mg chloride in a 50 mL sample.

The method is based on the formation of mercuric chloride when the solution suspected of containing hydrogen chloride is titrated with mercuric nitrate ($Hg(NO_3)_2$). The end point is reached when excess mercuric ion (Hg^{++}) is added. The end point when using just diphenylcarbazone as the indicator is the development of a blue-violet colour. The very limited ionization of mercuric chloride ($HgCl_2$) makes this titrimetric method for chloride ion possible. This method is also applicable to air samples suspected of containing hydrogen chloride after the sample has been collected in an absorber or impinger solution or to soil samples after extraction with water.

A suitable aliquot of sample, usually about 50 mL, is used. A mixed indicator consisting of 5 g of diphenylcarbazone and 0.5 g of bromophenol blue in 750 mL of isopropyl or 95 percent ethyl alcohol is used. The indicator is added to the sample and the pH is adjusted with 0.1 N nitric acid to the yellow end point. Bromophenol blue solution is blue above pH 4.6, yellow below pH 3, with the colour change range between these two values. The sample is titrated with 0.141 N mercuric nitrate. The relative standard deviation is 3.3 percent and the relative error is 2.9 percent. Bromide, cyanide, thiocyanate and iodide are determined as chloride. Chromate, ferric and sulphate ions interfere when present in excess of 10 mg/L. This method is fast and simple. The end point is easily determined except with turbid or highly coloured water which obscures the colour change.

11.3.3 Potentiometric Titration (AWWA 1976). This method is suitable for the detection of a range of 3 to 200 ppm chloride in water. This is equivalent to 0.15 to 10 mg chloride in a 50 mL sample.

A suitable volume of sample is collected. If necessary to remove interferences, the solution is acidified with nitric acid. It is titrated with silver nitrate using a glass and silver-silver chloride electrode system and determining the end point potentiometrically. The system is standardized with a standard sodium chloride solution. There are numerous interferences. Bromide, iodide and cyanide ions are determined as chloride. Ferricyanide, chromate and dichromate ions interfere and must be removed. When there are no interfering substances present, the precision and accuracy are about 2.5 percent of the amount of chloride present. If pretreatment is necessary to remove interferences, the precision and accuracy are reduced to 5 percent of the amount present. This method is suitable for coloured or turbid samples in which colour-indicated end points may be difficult to observe. This is the method of choice when ferric ions (Fe^{+++}), chromic phosphate ($CrPO_4$) and ferrous (Fe^{++}) and other heavy metal ions are present as well.

11.4 Qualitative Method for the Detection of Hydrochloric Acid in Water

The first qualitative test for hydrochloric acid in water should be a direct measurement of pH or a test with litmus paper. Methods described in Sections 11.2 and 11.3.1 may be used without a spectrophotometer, the colour development indicating the presence of chloride.

11.5 Quantitative Methods for the Detection of Hydrogen Chloride in Soil

11.5.1 Colourimetric Titration (Hesse 1972; Leithe 1971). This method is suitable for 0.15 to 10 mg chloride in the aliquot of extract taken for titration. When a 20 g sample is used for titration, this is equivalent to 7.5 to 500 ppm chloride.

A suitable weight, about 20 g, of 2 mm (sieve size) soil is weighed into a bottle and shaken with 100 mL of water for 30 minutes. The solution is removed and analyzed by any of the methods described in the preceding Sections.

11.5.2 Amperometric Titration (AWWA 1976). An aliquot of the extract containing 0.15 mg to 10 mg chloride is suitable for analysis by this method.

The soil extract is prepared as in Section 11.5.1 and analyzed as in Section 11.3.3.

11.6 Qualitative Method for the Detection of Hydrogen Chloride in Soil

The soil sample is prepared by extraction as described in Section 11.5. Litmus paper is used to indicate the presence of acid.

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Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/ alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight